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【SCOPE OF PATEMT CLAIMS】

1. A hydrogen generating method for generating hydrogen-containing gas by decomposing fuel containing an organic compound, wherein the method comprising providing a fuel electrode in contact with one surface of a partition membrane, supplying fuel containing an organic compound and water to the fuel electrode and providing an oxidizing electrode in contact with the other surface of the partition membrane, supplying an oxidizing agent to the oxidizing electrode, and providing electric energy from outside to the hydrogen generating cell with the fuel electrode serving as cathode and the oxidizing electrode as anode, thereby fuel containing the organic compound is decomposed and hydrogen-containing gas is generated on the fuel electrode.

2. The hydrogen generating method as described in any one of Claims 1, wherein the organic compound is alcohol.

3. The hydrogen generating method as described in Claim 2, wherein the alcohol is methanol.

4. The hydrogen generating method as described in any one of Claims 1 to 3, wherein the oxidizing agent is gas containing oxygen, or oxygen.

5. The hydrogen generating method as described in any one of Claims 1 to 3, wherein the oxidizing agent is liquid containing hydrogen peroxide.

6. The hydrogen generating method as described in any one of Claims 1 to 5, wherein running voltage between the

fuel electrode and the oxidizing electrode is 300 to 1000 mV, and thereby volume of hydrogen-containing gas evolution is adjusted.

7. The hydrogen generating method as described in Claim 6, wherein the running voltage between the fuel electrode and the oxidizing electrode is 400 to 600 mV.

8. The hydrogen generating method as described in any one of Claims 1 to 7, wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the supply volume of the oxidizing agent.

9. The hydrogen generating method as described in any one of Claims 1 to 8, wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the concentration of the oxygen-containing gas.

10. The hydrogen generating method as described in any one of Claims 1 to 9, wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the supply volume of fuel.

11. The hydrogen generating method as described in any one of Claims 1 to 10, wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the concentration of fuel containing the organic compound.

12. The hydrogen generating method as described in any one of Claims 1 to 11, wherein the running voltage

and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying electric energy applied to the fuel electrode and the oxidizing electrode.

13. The hydrogen generating method as described in any one of Claims 1 to 12, wherein fuel containing the organic compound is decomposed at temperature not higher than 100°C.

14. The hydrogen generating method as described in Claim 13, wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the temperature at range of 30 to 90°C.

15. A hydrogen generating system for generating hydrogen-containing gas by decomposing fuel containing an organic compound, wherein the system comprising providing partition membrane, a fuel electrode in contact with one surface of a partition membrane, means for supplying fuel containing an organic compound and water to the fuel electrode, an oxidizing electrode in contact with the other surface of the partition membrane, means for supplying an oxidizing agent to the oxidizing electrode, means for providing electric energy from outside to the hydrogen generating cell with the fuel electrode serving as cathode and the oxidizing electrode as anode, and means for generating and withdrawing the hydrogen-containing gas on the fuel electrode.

16. The hydrogen generating system as described in Claim 15, wherein the partition membrane is a proton

conducting solid electrolyte membrane.

17. The hydrogen generating system as described in Claim 16, wherein the proton conducting solid electrolyte membrane is a perfluorocarbon sulfonate-based solid electrolyte membrane.

18. The hydrogen generating system as described in any one of Claims 15 to 17, wherein the catalyst applied to the fuel electrode is made of platinum-ruthenium alloy supported by carbon powder serving as a base.

19. The hydrogen generating system as described in any one of Claims 15 to 18, wherein the catalyst applied to the oxidizing electrode is made of platinum supported by carbon powder serving as a base.

20. The hydrogen generating system as described in any one of Claims 15 to 19, wherein running voltage between the fuel electrode and the oxidizing electrode is 300 to 1000 mV.

21. The hydrogen generating system as described in Claim 20, wherein the running voltage between the fuel electrode and the oxidizing electrode is 400 to 600 mV.

22. The hydrogen generating system as described in any one of Claims 15 to 21, wherein the operation temperature is not higher than 100°C.

23. The hydrogen generating system as described in Claim 22, wherein the operation temperature is between 30 and 90°C.

24. The hydrogen generating system as described in

any one of Claims 15 to 23 comprising means for circulating fuel containing an organic compound.

25. The hydrogen generating system as described in any one of Claims 15 to 24 comprising a carbon dioxide absorbing portion for absorbing carbon dioxide contained in the generated hydrogen-containing gas.

【DOCUMENT NAME】 SPECIFICATION

【TITLE OF THE INVENTION】

HYDROGEN GENERATING METHOD AND HYDROGEN GENERATING SYSTEM BASED ON THE METHOD

【TECHNICAL FIELD】

[0001] The present invention relates to a method for decomposing fuel comprising an organic compound into a hydrogen-containing gas at a low temperature, and a hydrogen generating system based on the method.

BACKGROUND ART

[0002] Recently, people have increasingly directed their attention to the pollution of environment or the exhaustion of natural resources, and to the development of measures to cope with those problems. As one such countermeasure, the development of fuel cells have been actively pursued. Among such fuel cells, there are phosphoric acid fuel cells (PAFC) and polymer electrolyte fuel cells (PEFC). Utilizing hydrogen as fuel, those fuel cells require a conversion system capable of converting hydrocarbon or methanol which serves as a material into hydrogen, and the development of an effective conversion system has remained a particularly important technical challenge in the development efforts of those fuel cells.

[0003] Materials upon which studies have been performed to convert them into hydrogen to drive PEFCs for vehicles include, for example, methanol, dimethyl ether (DME), ethanol, natural gas, propane, gasoline, etc. Among them,

the most notable advancement is observed in the conversion of methanol into hydrogen, because methanol requires the lowest temperature for its conversion. Currently, three methods have been proposed for methanol conversion: water vapor-based conversion, partial oxidization-based conversion, and combination of the two methods (see Non-Patent Publication 1).

[0004] 【Non-Patent Publication 1】 Watanabe, M., "Development of PEFC and its commercialization," pp. 141-166, May 28, 1999, Assoc. Technol. Information.

[0005] The water vapor-based conversion can be represented by the following reaction formula:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

This is an endothermic reaction occurring at 200 to 300°C.

[0006] The partial oxidization-based conversion can be represented, when air is used as oxidizing gas, by the following reaction formula:

$$CH_3OH + 1/2O_2 + 2N_2 \rightarrow CO_2 + 2H_2 + 2N_2$$

This is an exothermic reaction occurring at 200 to 600°C.

[0007] The combinational conversion (representative example) can be represented, when air is used as oxidizing gas, by the following reaction formula:

$$CH_3OH + 1/3O_2 + 4/3N_2 + 1/3H_2O \rightarrow CO_2 + 7/3H_2 + 4/3N_2$$

This is an exothermic reaction where heat is generated about one third what is generated during the partial

oxidization-based conversion. The reaction occurs at 400 to 600°C.

[0008] As an alternative to the above method, an invention provides a hydrogen generating system for generating hydrogen highly efficiently utilizing, as a material, hydrocarbon fuel such as natural gas, LPG, gasoline, naphtha, kerosene, etc., and water in order to provide resulting hydrogen, for example, to a hydrogen exploiting device such as a fuel cell (see Patent Publication 1). According to the invention, the system "comprises, at least, a hydrocarbon fuel supply portion, a combustion portion, a water supply portion, a gas mixing portion where fuel and water or water vapor are mixed to produce a mixed gas to be converted, and a conversion portion filled with a conversion catalyst, and is characterized in that the gas to be converted is converted, under the catalytic action of the conversion catalyst, into gas containing hydrogen, and that combustion gas waste generated by the combustion portion is used to directly heat, only through partition walls, at least the gas mixing portion and the conversion portion." According to this system, the conversion temperature is high, that is, about 700°C.

【Patent Publication 1】 Japanese Patent Publication No. 3473900 (See Claim 1, and paragraphs [0001], [0017] and [0022] of the cited patent document).

[0009] As seen from the two illustrative methods presented above, for generating hydrogen conversion must occur at a

high temperature not lower than 200°C, and, in addition, those conventional methods have a number of additional problems: intoxication of the conversion catalyst, admixture of CO with the conversion gas (hydrogen-containing gas) which must be removed, and admixture of air with the conversion gas which is generated by partial oxidization or by the combinational method.

[0010] Conventionally, there exist inventions disclosing a hydrogen evolution method and a hydrogen evolution apparatus by which hydrogen is evolved at a low temperature and a low pressure without using a catalyst (see Patent Documents 2 and 3). These documents describe a "method for steam reforming of chain hydrocarbon" and a "hydrogen evolution apparatus". According to the steam reforming method, a direct-current pulse discharge is effected in a mixture gas containing gaseous chain hydrocarbon and steam to allow these elements to react with each other in order to evolve hydrogen and carbon monoxide. On the other hand, the hydrogen evolution apparatus includes a discharge electrode constituted by a bundle of a plurality of conductive fibers. This discharge electrode has capillary tubes interposed between the conductive fibers. The capillary tubes supply a material containing water and at least one substance selected from hydrocarbon and an organic oxygenated compound. With this configuration, the discharge electrode conducts pulse discharge to induce a reaction of the material supplied by the capillary tubes,

thereby evolving hydrogen. Such being the case, the steam reforming method and the hydrogen evolution apparatus set forth entail such an issue: In order to evolve hydrogen, electric energy must be input using the discharge electrode, and in this case, a large quantity of electric energy must be supplied from outside.

【Patent Publication 2】 Japanese Patent Laid-Open Publication No. 2001-335302 (See Claim 1, Claim 8, and paragraphs [0007], [0025])

【Patent Publication 3】 Japanese Patent Publication No. 3476811 (See Claim 1, and paragraphs [0091], [0112])

[0011] Further, an invention of method for generating hydrogen electrochemically (see Patent Publications 4 and 6) and an invention of a fuel cell utilizing hydrogen generated by such an electrochemical method (see Patent Publications 5·to 7) have been known.

【Patent Publication 4】 Japanese Patent Publication No. 3328993

【Patent Publication 5】 Japanese Patent Publication No. 3360349

【Patent Publication 6】 United States Patent Publications Nos. 6,299,744, 6,368,492, 6,432,284, and 6,533,919, and United States Patent Application No. 2003/0226763

【Patent Publication 7】 Japanese Patent Laid-Open Publication No. 2001-297779

[0012] Patent Publication 4 cited above describes (Claim 1), "a method for generating hydrogen comprising providing a

pair of electrodes on the two opposite surfaces of a cation exchange membrane, contacting a fuel containing at least methanol and water with one electrode having a catalyst, applying a voltage between the pair of electrodes so that electrons are withdrawn from the electrodes thereby causing a reaction to occur on the electrodes whereby hydrogen ions are generated from methanol and water, and allowing hydrogen ions to be converted on the other electrode, being supplied with electrons, into hydrogen molecules." The same patent document discloses another method (paragraphs [0033] to [0038]) for selectively generating hydrogen using a conversion system, the method comprising supplying water or water vapor together with methanol which serves as a fuel, applying a voltage via an external circuit to cause electrons to be withdrawn from a fuel electrode, so that reaction represented by $CH_3OH + 2H_2O \rightarrow CO_2 + 6e^- + 6H^+$ occurs on the fuel electrode, and allowing hydrogen ions thus produced to pass through a cation exchange membrane to reach the opposite electrode where the hydrogen ions undergo reaction represented by $6H^+ + 6e^- \rightarrow 3H_2$. Further, Patent Publication 5 cited above describes (paragraphs [0052] to [0056]) a fuel cell which utilizes hydrogen generated by a method as described above.

According to the inventions described in Patent Publications 4(paragraph [0042]) and 5(paragraph [0080]) cited above, it is possible to generate hydrogen at a low temperature. However, the methods described in those

inventions are obviously different from the hydrogen generating method of the present invention and hydrogen generating system of the present invention based on the method which will be given below in following points: those methods require the application of voltage, and hydrogen is generated on the electrode opposite to the electrode (fuel electrode) to which fuel is supplied, and no oxidizing agent is supplied to the opposite electrode.

[0013] This holds true also for the inventions disclosed by Patent Publication 6 cited above similarly to Patent Publications 4 and 5 cited above. Those inventions use a system for generating hydrogen where protons generated on anode 112 serving as fuel electrode pass through partition membrane 110 to reach cathode 114 opposite to the anode, and according to the system, voltage from DC power source 120 is applied between anode (fuel electrode) and cathode (opposite electrode) to decompose organic fuel such as methanol or the like electrochemically. In addition, hydrogen is generated on the electrode opposite to the fuel electrode.

[0014] Patent Publication 7 cited above discloses a fuel cell system incorporating a hydrogen generating unit. According to the disclosure (Claim 1) of the invention, "Liquid fuel containing alcohol and water is supplied to porous electrode 1 (fuel electrode), air is supplied to gas diffusion electrode 2 (oxidizing agent-applied electrode) opposite to electrode 1, and a load is inserted between a

terminal leading to porous electrode 1 and another terminal leading to gas diffusion electrode 2 to achieve electric connection allowing a positive voltage to be applied to porous electrode 1 via the load from gas diffusion electrode 2 which corresponds to the positive electrode of MEA2 capable of acting as a conventional fuel cell." The same patent Publication further adds (paragraph [0007]), "As a result, alcohol reacts with water to produce carbon dioxide gas and hydrogen ion, the hydrogen ion passes through an electrolyte membrane 5 to reach a gas diffusion electrode 6 located centrally where the hydrogen ion is converted into hydrogen gas. On the opposite surface of gas diffusion electrode 6 in contact with another electrolyte layer 7, there arises another electrode reaction where hydrogen gas is reconverted into hydrogen ion, and hydrogen ions migrate through electrolyte layer 7 to reach another gas diffusion electrode 2 where hydrogen ions react with oxygen in air to produce water." Thus, with this system, electric energy generated by a fuel cell is utilized to generate hydrogen on the hydrogen generating electrode which is then supplied to the fuel cell. Moreover, the system is the same with those described in the patent Publications 2 to 4 cited above in that hydrogen is generated on the electrode opposite to the fuel electrode.

[0015] There are some other known methods for generating hydrogen (Japanese Unexamined Patent Application

Publications Nos. 6-73582 (Claims 1 to 3, paragraph [0050]) and 6-73583 (Claims 1 and 8, paragraphs [0006] and [0019]). According to the inventions, a reaction system with a partition membrane is used where anode (electrode A) and cathode (electrode B) are placed opposite to each other with a proton conducting membrane (ion conductor) inserted therebetween, and where alcohol (methanol) is oxidized with or without concomitant application of voltage, or with concomitant uptake of electric energy. All those methods, however, are based on a method whereby alcohol is oxidized by means of an electrochemical cell (the reaction product includes carbonic diester, formalin, methyl formate, dimethoxymethane, etc.), and not on a method whereby alcohol is converted by reduction into hydrogen."

【Patent Publication 8】 (Japanese Patent Application No. 6-73582 (Claims 1 to 3, paragraph [0050])

【Patent Publication 9】 Japanese Patent Publication No. 6-73583 (Claims 1 and 8, paragraphs [0006] and [0019]).

【DISCLOSURE OF THE INVENTION】

【Problems to be Solved by the Invention】

[0016] With a view to give a solution to the above problems, the present invention aims to provide a hydrogen generating method whereby one can decompose fuel containing an organic compound at a low temperature requiring a little volume of electric energy supplied from outside, to generate gas in which admixture of nitrogen, etc., is insignificant, and a hydrogen generating system based on the hydrogen generating method.

Namely, the present invention aims to provide a hydrogen gas having energy more than the electric energy input. Here, we emphasize that the object of the present invention is to provide a hydrogen gas having a chemical energy more than the electric energy input, and the invention never ignores the law of conservation of energy, principle of thermodynamics. On the whole, part of an organic fuel is oxidized, and therefore, the input electric energy involving the chemical energy consumed by the oxidation of the organic fuel results in 100% or less of energy efficiency. According to the present invention, in an attempt to clarify the difference with respect to the conventional hydrogen generation through water electrolysation, the ratio of a chemical energy of an evolved hydrogen to an input electric energy is used as energy efficiency.

[0017] In the course of the development of a direct methanol fuel cell using methanol as fuel, the present inventors found in the first place that hydrogen is evolved from a fuel electrode side of a fuel cell under open circuit condition, where the direct methanol fuel cell is not supplied with current from outside, and the voltage of the fuel electrode and an air electrode is constant. The present inventors therefore filed a Japanese Patent Application No. 2003-433710 for this finding. The present inventors further explored the phenomenon cited above, and found that hydrogen is evolved not only under the open circuit condition, where current is not supplied from outside but also under the condition where current is

withdrawn to outside as a cell.

The inventors achieved the present invention based on the results of further investigation. According to the results, it was determined that hydrogen is evolved under charging condition, that is, under electrolytic condition, in addition to the open circuit and discharging conditions, and that the hydrogen is evolved more than the input electric energy depending on operation conditions.

[0018] Proposed to give a solution to the problems, the present invention can be reduced to following constitutive elements.

(1) A hydrogen generating method for generating hydrogen-containing gas by decomposing fuel containing an organic compound, wherein the method comprising providing a fuel electrode in contact with one surface of a partition membrane, supplying fuel containing an organic compound and water to the fuel electrode and providing an oxidizing electrode in contact with the other surface of the partition membrane, supplying an oxidizing agent to the oxidizing electrode, and providing electric energy from outside to the hydrogen generating cell with the fuel electrode serving as cathode and the oxidizing electrode as anode, thereby fuel containing the organic compound is decomposed and hydrogen-containing gas is generated on the fuel electrode.

(2) The hydrogen generating method as described in any one of paragraph (1), wherein the organic compound is alcohol.

(3) The hydrogen generating method as described in paragraph (2), wherein the alcohol is methanol.

(4) The hydrogen generating method as described in any one of paragraphs (1) to (3), wherein the oxidizing agent is gas containing oxygen, or oxygen.

(5) The hydrogen generating method as described in any one of paragraphs (1) to (3), wherein the oxidizing agent is liquid containing hydrogen peroxide.

(6) The hydrogen generating method as described in any one of paragraphs (1) to (5), wherein running voltage between the fuel electrode and the oxidizing electrode is 300 to 1000 mV, and thereby volume of hydrogen-containing gas evolution is adjusted.

(7) The hydrogen generating method as described in paragraph (6), wherein the running voltage between the fuel electrode and the oxidizing electrode is 400 to 600 mV.

(8) The hydrogen generating method as described in any one of paragraphs (1) to (7), wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the supply volume of the oxidizing agent.

(9) The hydrogen generating method as described in any one of paragraphs (1) to (8), wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the concentration of the oxygen-containing gas.

(10) The hydrogen generating method as described in

any one of paragraphs (1) to (9), wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the supply volume of fuel.

(11) The hydrogen generating method as described in any one of paragraphs (1) to (10), wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the concentration of fuel containing the organic compound.

(12) The hydrogen generating method as described in any one of paragraphs (1) to (11), wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying electric energy applied to the fuel electrode and the oxidizing electrode.

(13) The hydrogen generating method as described in any one of paragraphs (1) to (12), wherein fuel containing the organic compound is decomposed at temperature not higher than 100°C.

(14) The hydrogen generating method as described in paragraph (13), wherein the running voltage and/or the evolution volume of hydrogen-containing gas are/is adjusted by varying the temperature at range of 30 to 90°C.

(15) A hydrogen generating system for generating hydrogen-containing gas by decomposing fuel containing an organic compound, wherein the system comprising providing partition membrane, a fuel electrode in contact with one surface of a partition membrane, means for supplying fuel containing an organic compound and water to the fuel

electrode, an oxidizing electrode in contact with the other surface of the partition membrane, means for supplying an oxidizing agent to the oxidizing electrode, means for providing electric energy from outside to the hydrogen generating cell with the fuel electrode serving as cathode and the oxidizing electrode as anode, and means for generating and withdrawing the hydrogen-containing gas on the fuel electrode.

(16) The hydrogen generating system as described in paragraph (15), wherein the partition membrane is a proton conducting solid electrolyte membrane.

(17) The hydrogen generating system as described in paragraph (16), wherein the proton conducting solid electrolyte membrane is a perfluorocarbon sulfonate-based solid electrolyte membrane.

(18) The hydrogen generating system as described in any one of paragraphs (15) to (17), wherein the catalyst applied to the fuel electrode is made of platinum-ruthenium alloy supported by carbon powder serving as a base.

(19) The hydrogen generating system as described in any one of paragraphs (15) to (18), wherein the catalyst applied to the oxidizing electrode is made of platinum supported by carbon powder serving as a base.

(20) The hydrogen generating system as described in any one of paragraphs (15) to (19), wherein running voltage between the fuel electrode and the oxidizing electrode is 300 to 1000 mV.

(21) The hydrogen generating system as described in paragraph (20), wherein the running voltage between the fuel electrode and the oxidizing electrode is 400 to 600 mV.

(22) The hydrogen generating system as described in any one of paragraphs (15) to (21), wherein the operation temperature is not higher than 100°C.

(23) The hydrogen generating system as described in paragraph (22), wherein the operation temperature is between 30 and 90°C.

(24) The hydrogen generating system as described in any one of paragraphs (15) to (23) comprising means for circulating fuel containing an organic compound.

(25) The hydrogen generating system as described in any one of paragraphs (15) to (24) comprising a carbon dioxide absorbing portion for absorbing carbon dioxide contained in the generated hydrogen-containing gas.

[0019] The hydrogen generating system comprise means for supplying fuel and oxidizing agent to the hydrogen generating unit and electrolysis means for providing electric energy to the hydrogen generating cell. Further, the hydrogen generating system cited above is capable of monitoring the running voltage of its hydrogen generating cell and/or the evolution volume of hydrogen-containing gas, and adjusting, based on the monitor result, the supply volumes of fuel and oxidizing agent or their concentrations, and the magnitude of electric energy provided to the hydrogen generating cell. Still, the basic composition of

a hydrogen generating cell constituting the hydrogen generating system consists of a fuel electrode provided on one surface of a partition membrane, a structure for supplying fuel to the fuel electrode, an oxidizing electrode provided to the other surface of the partition membrane, and another structure for supplying an oxidizing agent to the oxidizing electrode.

【Effect of the Invention】

[0020] Employment of the inventive hydrogen generating method or a hydrogen generating system based on the method makes it possible to convert fuel into hydrogen at a temperature close to room temperature or 10°C or lower which is far lower than the temperature required for conventional fuel conversion, which allows the economical use of energy necessary for running the system. Furthermore, according to the inventive method or a system based on the method, the hydrogen-containing gas generated is only marginally contaminated with nitrogen, and practically devoid of CO, and thus it is possible to obtain a comparatively high yield of hydrogen, and to dispense with a step for removing CO from the gas.

[0020] By providing a little electric energy to the hydrogen generating cell from outside to allow it to generate hydrogen, the system is advantageous in that hydrogen generated exceeds in volume the hydrogen obtainable as a result of the consumption of the injected electric energy.

Furthermore, it is possible to control the process as appropriate by monitoring the voltage of the hydrogen generating cell and/or the evolution volume of hydrogen-containing gas, which allows the compaction of the system and the low cost running of the system.

【BEST MODE FOR CARRYING OUT THE INVENTION】

[0021] The most preferred embodiments in the execution of the present invention will be illustrated below.

[0022] The hydrogen generating cell constituting the hydrogen generating system of the invention is basically composed of a partition membrane, a fuel electrode provided on one surface of partition membrane and an oxidizing electrode provided on the other surface of partition membrane as described above. The element configured as described above may be represented by an MEA (membrane/electrode assembly) used in a direct methanol fuel cell.

[0023] The method for fabricating an MEA is not limited to any specific one, but a method similar to a conventional one may be employed wherein a fuel electrode and an oxidizing electrode (air electrode) with a partition membrane inserted therebetween are compressed at a high temperature to be assembled.

[0024] Suitable partition membranes may include a proton conducting solid electrolyte membrane which has been used as a polymer electrolyte membrane of a fuel cell. The proton conducting solid electrolyte membrane preferably

includes a membrane based on perfluorocarbon sulfonate having sulfonic acid group such as Nafion provided by Dupont.

[0025] The fuel electrode or oxidizing (air) electrode is preferably an electrode which is conductive and has a catalytic activity. Production of such an electrode may be achieved by applying a catalyst paste onto a gas diffusion layer and drying the paste, wherein the paste is comprised of a catalyst obtained by blending a precious metal with carbon powder serving as a base, a binding agent such as a PTFE resin, and an ion conductivity conferring substance such as Nafion solution.

The gas diffusion layer is preferably made of a carbon paper treated to be water-repellent.

The catalyst to be applied to fuel electrode is not limited to any specific one, but is preferably a platinum-ruthenium alloy supported by carbon powder serving as a base.

The catalyst applied to air electrode is not limited to any specific one, but is preferably platinum supported by carbon powder serving as a base.

[0026] For a hydrogen generating system configured as described above, when fuel containing an organic compound such as an aqueous solution of methanol is supplied to the fuel electrode, and aerial air containing oxygen is supplied to the air electrode, gas containing hydrogen evolves on the fuel electrode under specified conditions.

[0027] The hydrogen generating method of the invention is quite different from conventional hydrogen generating methods, and it is still difficult at present to explain the mechanism. The hypothesis which is currently thought most likely to be true will be described below, but it can not be denied that the hypothesis would be upset by new reactions which will shed new light to the phenomenon.

[0028] According to the hydrogen generating method of the present invention, gas containing hydrogen at 80% or higher evolves, at a temperature as low as 30 to 90°C, from the fuel electrode which receives the supply of methanol and water as will be described below. The evolution of gas depends on the running voltage between the two electrodes. Base on these results, the most likely explanation of the mechanism underlying the evolution of hydrogen is as follows. For brevity, description will be given below on the premise that the cell is kept under circuit-open condition.

[0029] Let's assume for example that methanol is applied, as fuel. Firstly proton is likely to be generated on the fuel electrode by virtue of a catalyst, as is the case with a DMFC.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad ....(1)$$

When Pt-Ru is used as a catalyst, methanol is adsorbed to the surface of Pt, and undergoes a series of electrochemical oxidization reactions as described below, resulting in the production of chemical species firmly

adhered to the surface of the catalyst ultimately leading to reaction (1) described above, so it is contended ("Handbook of Electric Cell," Feb 20, 2001, p. 406, Maruzen, 3rd edition).

$CH_3OH + Pt \rightarrow Pt\text{-}(CH_3OH)ads$

$\rightarrow Pt\text{-}(CH_2OH)ads + H^+ + e^-$

$Pt\text{-}(CH_2OH)ads \rightarrow Pt\text{-}(CHOH)ads + H^+ + e^-$

$Pt\text{-}(CHOH)ads \rightarrow Pt\text{-}(COH)ads + H^+ + e^-$

$Pt\text{-}(COH)ads \rightarrow Pt\text{-}(CO)ads + H^+ + e^-$

To further oxidize Pt-(CO)ads, it is necessary to prepare (OH)ads from water.

$Ru + H_2O \rightarrow Ru\text{-}(H_2O)ads$

$\rightarrow Ru\text{-}(OH)ads + H^+ + e^-$

$Ru\text{-}(OH)ads + Pt\text{-}(CO)ads \rightarrow Ru + Pt + CO_2 + H^+ + e^-$

[0030] For a DMFC, H^+ (proton) generated on the fuel electrode as a result of the reaction represented by formula (1) migrates through a proton conducting solid electrolyte membrane to reach the oxidizing electrode where it reacts with oxygen-containing gas or oxygen supplied to the oxidizing electrode as represented by the following reaction formula.

$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ ....(2)

Since the present invention works to provide electric energy from outside (e^- is provided to fuel electrode from outside) to the hydrogen generating cell with the fuel electrode serving as cathode and the oxidizing electrode as anode and e^- is not provided to the

oxidizing electrode from outside. Therefore, for the reaction represented by formula (2) to occur, it is necessary to supply e^- to the oxidizing electrode from a different reaction.

[0031] By the way, with regard to a DMFC using a proton conducting solid electrolyte membrane such as Nafion, there has been known a phenomenon called methanol crossover, that is, the crossover of methanol from the fuel electrode to the oxidizing electrode. Thus, it is possible that crossed methanol undergoes electrolytic oxidization represented by the following formula on the oxidizing electrode.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad ....(3)$$

If the reaction represented by formula (3) occurs, e^- produced as a result of the reaction is supplied to allow the reaction represented by formula (2) to occur there.

[0032] The H^+ (proton) produced as a result of the reaction represented by formula (3) migrates through the proton conducting solid electrolyte membrane to reach the fuel electrode to undergo there a reaction represented by the following formula to produce hydrogen.

$$6H^+ + 6e^- \rightarrow 3H_2 \quad ....(4)$$

In this sequence of reactions, the transfer of H^+ and e^- produced as a result of the reaction represented by formula (1) on the fuel electrode to the oxidizing electrode and the transfer of H^+ and e^- produced as a result of the reaction represented by formula (3) on the

oxidizing electrode to the fuel electrode are likely to be apparently canceled out by each other.

Then, on the oxidizing electrode there arises reaction as represented by formula (2) based on H^+ and e^- produced as a result of the reaction represented by formula (3), while on the fuel electrode there arises reaction as represented by formula (4) based on H^+ and e^- produced as a result of the reaction represented by formula (1).

[0033] Assumed that reactions represented by formulas (1) and (4) occur on the fuel electrode while reactions represented by formulas (2) and (3) occur on the oxidizing electrode, the net balance of chemical reactions is likely to be expressed by the following formula (5).

$$2CH_3OH + 2H_2O + 3/2O_2 \rightarrow 2CO_2 + 3H_2O + 3H_2 \quad ....(5)$$

The theoretical efficiency of this reaction is 59% (calorific value of 3 mol. hydrogen/calorific value of 2 mol. methanol).

[0034] As will be described later in relation to Example, a reaction system exposed to a higher temperature is more apt to generate hydrogen, and thus endothermic reactions (1) and (3) are likely to proceed in the arrow-indicated direction, being supplied heat from outside via other exothermic reactions.

Methanol not only undergoes reactions as represented by formulas (1) and (3), but is also subject, as a result of crossover, to the subsidiary reaction where methanol permeating from the fuel electrode is oxidized by

oxygen on the surface of catalyst coated on the air electrode as represented by the following formula.

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \quad \ldots.(6)$$

Since the reaction of formula (6) is an exothermic reaction, heat generated by this reaction is most likely to be used to allow reactions represented by formulas (1) and (3) to occur.

[0035] With regard to a hydrogen generating cell according to the present invention, hydrogen is likely to be generated depending on the same mechanism as in the open-circuit condition. However, in contrast with the open-circuit condition, it is necessary with this system for H^+ corresponding in volume to electrolyte current to migrate from the oxidizing electrode to the fuel electrode in order to establish the neutralized electrical condition of the cell. Therefore, it is likely that reaction of formula (4) rather than reaction of formula (1) will occur on the fuel electrode while reaction of formula (3) rather than reaction of formula (2) will occur on the oxidizing electrode.

To put it more specifically, with regard to the charging condition where the fuel electrode serves as cathode while the oxidizing electrode serves as anode, electric energy is supplied from outside (e^- is supplied from outside to the fuel electrode). Then, basically electrolysis occurs in the system. As electric energy supplied (voltage applied) is increased, more hydrogen will

be produced. This is probably because as more e^- is supplied from outside to the fuel electrode, oxidization of methanol represented by formula (3) and reaction represented by formula (4) ($6H^+ + 6e^- \rightarrow 3H_2$) will be more enhanced as will become apparent from the description given below in relation to Example.

[0036] However, as will be described later, the energy efficiency of the system becomes high when applied voltage (running voltage) is at a low range of 400 to 600 mV. This is probably because the oxidation of methanol permeated to air electrode as represented by formula (6) is suppressed, evolution reaction of H^+ as represented by formula (3) becomes dominant, and the H^+ undergoes reaction represented by formula (4) to produce hydrogen in the same manner as described above even in the case of open-circuit condition or discharging condition where electric energy is not provided from outside. Evolution of hydrogen in the charging condition is likely to be generated depending on the same mechanism as in the open-circuit condition and discharging condition as well as on the electric energy supplied from outside.

[0037] The meaning of the potential of the cell will be described here. Generally, the voltage of a cell having two electrodes with an electrolyte membrane inserted therebetween is determined by the difference between the two electrodes of chemical potentials of ions which serve as conductors in electrolyte.

If polarizations at the two electrodes are ignored, the voltage in question indicates the difference between the two electrodes of chemical potentials of hydrogen, in other words, partial pressures of hydrogen, since this cell uses a proton (hydrogen ion) conducting solid electrolyte membrane.

[0038] According to the invention, as will be described later in relation to Example, if running voltage is in a certain range, this indicates the evolution of hydrogen on the fuel electrode. Thus, if the difference of chemical potentials of hydrogen between the two electrodes falls within a certain range, reactions as represented by formulas (1) to (6) cited above will proceed which will result in the production of hydrogen.

[0039] According to the present invention, it is possible to adjust the volume of gas containing hydrogen thereby adjusting the running voltage between the fuel electrode and oxidizing electrode with applying a little electric energy to the hydrogen generating cell from outside.

The running voltage is preferably to be adjusted to 300 to 1000mV(energy efficiency is high at 400 to 600 mV).

[0040] As will be described below in relation of Example, it is possible to adjust the running voltage and/or the evolution volume (rate of hydrogen evolution) of hydrogen-containing gas by varying the supply volume of an oxidizing agent (oxygen-containing gas or oxygen, or hydrogen peroxide-containing liquid), or the oxygen concentration of

oxygen-containing gas, or the supply volume of compound-containing fuel, or the concentration of organic compound-containing fuel, or electric energy supplied to the system (or current supplied to the system, or by varying the voltage of the system using a constant-voltage power source, for example, so-called potentiostat).

[0041] Since according to the hydrogen generating method of the invention or to a hydrogen generating system based on the method, it is possible to decompose organic compound-containing gas at 100°C or lower, the temperature at which the system can be operated is made 100°C or lower. The operation temperature is preferably 30 to 90°C. This is because, when the operation temperature is adjusted to be between 30 and 90°C, it will become possible to adjust the running voltage, and/or the evolution volume of hydrogen-containing gas as will be described later in relation to Example.

Incidentally, for a hydrogen generating cell based on conventional fuel conversion technology, the operation temperature should be kept at 100°C or higher. At this temperature range, water will become vapor and organic compound-containing fuel become gas, and even when hydrogen evolves under this condition, it is necessary to provide means specifically adapted for separating hydrogen. The system of the present invention is also advantageous in this point.

Indeed, there will arise a problem as described

above, when organic compound-containing fuel is decomposed at 100°C or higher. But a hydrogen generating system of the invention may be operated at a temperature slightly above 100°C if there be need to do so.

[0042] As long as based on the putative principle, the organic compound-containing fuel may be liquid or gaseous fuel capable of producing proton as a result of electrochemical oxidization that can pass through a proton conductive partition membrane, and liquid fuel containing alcohol such as methanol is preferred. Since the organic compound-containing fuel is supplied with water, an aqueous solution of alcohol, particularly aqueous solution of methanol is preferred. The aqueous solution of methanol cited above as a preferred example of fuel is an aqueous solution containing at least methanol, and its concentration of methanol at a region where hydrogen-containing gas evolves may be arbitrarily determined as needed.

[0043] Suitable oxidizing agents may include gaseous or liquid oxidizing agents. Suitable gaseous oxidizing agents may include oxygen-containing gas or oxygen. The concentration of oxygen in oxygen-containing gas is preferably chosen to be 10% or higher. Suitable liquid oxidizing agents may include hydrogen peroxide-containing liquid.

[0044] For a hydrogen generating system of the invention, since the fraction of fuel converted into hydrogen is

rather small, it is desirable to provide fuel circulating means to improve thereby the fraction of fuel to be converted into hydrogen.

[0045] The hydrogen generating system of the invention has means for withdrawing hydrogen-containing gas provided on the fuel electrode. The means is preferably so constructed as to be able to recover carbon dioxide as well as hydrogen. Since the system operates at a temperature as low as 100°C or lower, it is possible to attach a carbon dioxide absorbing portion for absorbing carbon dioxide contained in hydrogen-containing gas to the system by simple means.

Next, illustrative examples (examples of hydrogen generation) of the present invention will be presented. However, the fractions of catalysts, PTFE, Nafion, etc., and the thickness of catalyst layer, gas diffusion layer and electrolyte membrane are not limited to the values cited in the examples, but may take any appropriate values.

【EXAMPLE 1】

[0046] Hydrogen generating cells described in Example 1 have the same structure as that of representative DMFCs.

The structure of the hydrogen generating cell is outlined in Fig. 1.

The electrolyte membrane consists of a proton conducting electrolyte membrane provided by Dupont (Nafion 115); and the air electrode is obtained by immersing carbon paper (Toray) in a solution where polytetrafluoroethylene is dispersed at 5%, and baking the paper at 360°c to make

it water-repellent, and coating, on one surface of the paper, air electrode catalyst paste comprised of air electrode catalyst (carbon-supported platinum, Tanaka Precious Metal), fine powder of PTFE, and 5% Nafion solution (Aldrich). Thus, the air electrode exists as a gas diffusion layer with air electrode catalyst. In the preparation of the air electrode catalyst paste, the percent contents by weight of air electrode catalyst, PTFE, and Nafion were made 65%, 15% and 20%, respectively. The loading level of catalyst of the air electrode prepared as above was 1 mg/cm^2 in terms of the weight of platinum per unit area.

[0047] Another carbon paper was similarly treated to be made water-repellent. One surface of the paper was coated with fuel electrode catalyst paste comprised of fuel electrode catalyst (carbon-supported platinum-ruthenium, Tanaka Precious Metal), fine powder of PTFE, and 5% Nafion solution. Thus, the fuel electrode exists as a gas diffusion layer with fuel electrode catalyst. In the preparation of the fuel electrode catalyst paste, the percent contents by weight of fuel electrode catalyst, PTFE, and Nafion were made 55%, 15% and 30%, respectively. The loading level of catalyst of the fuel electrode prepared as above was 1 mg/cm^2 in terms of the weight of platinum-ruthenium per unit area.

[0048] The electrolyte membrane, gas diffusion layer with air electrode catalyst and gas diffusion layer with fuel

electrode catalyst were laid one over another to be not-pressed at 140°C under a pressure of 100 kg/cm^2 so that they were assembled to form an MEA. The MEA prepared as above had an active electrode area of 60.8 cm^2. The thicknesses of air and fuel electrode catalyst layers were practically the same about 30 μm, and the thicknesses of air and fuel electrode gas diffusion layers were similarly the same about 170 μm.

[0049] The MEA was further provided on its both surfaces with flow passages through which air can flow and fuel can flow, and was enclosed from outside with an air electrode separator and a fuel electrode separator respectively both made of graphite into which phenol resin is impregnated, in order to prevent the leak of gas from the MEA. To further ensure the seal of MEA against the leak of fuel and air, MEA was surrounded with silicon-rubber made packing.

[0050] The hydrogen generating cell was placed in an electric furnace where hot air was circulated. The cell was operated while the temperature being kept at 50°C with the flow of air to the air electrode kept at 10 to 80 ml/min and the flow of 1M aqueous solution of methanol (fuel) to the fuel electrode kept at 5 ml/min. Then, while the current flowing between the air electrode and the fuel electrode being varied by means of a DC power source from outside, the running voltage between the fuel electrode and the air electrode, the volume of gas evolved from the fuel electrode and gas composition were monitored and analyzed.

The energy efficiency of charging condition was defined as a ratio of the chemical energy of hydrogen evolved to the electric energy supplied from outside. The concentration of hydrogen in the generated gas was determined by gas chromatography, and rate of hydrogen evolution also determined.

The energy efficiency of a charging condition was calculated based on the following equation:

Energy efficiency (%) = (combustion heat of H_2/electric energy applied) x 100

Combustion heat (kJ) of H_2 per minute = (rate of H_2 evolution ml/min/24.47/1000) x 286 kJ/mol [HHV]

Electric energy (kJ) per minute = (voltage mV/1000 x current A x 60 sec)Wsec/1000

[0051] Relation of the rate of hydrogen evolution with the current density applied in the test is shown in Fig. 2.

It was found that the efficiency of hydrogen evolution (efficiency of hydrogen evolution relative to electric energy supplied) becomes equal to or more than 100% (100% efficiency of hydrogen evolution is represented by the dashed line in Fig. 2) in certain areas when the current density is kept not more than 40 mA/cm^2. This suggests that it is possible to obtain hydrogen whose energy content is larger than the electric energy supplied from outside by operating the cell in those areas.

[0052] Fig. 3 shows a graph for indicating relationship between the rate of hydrogen evolution and the running

voltage, both adapted from the results of Fig. 2.

From this it was found that the rate of hydrogen evolution (volume of hydrogen evolution) tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 400 mV, and the rate of hydrogen evolution becomes virtually constant when the running voltage becomes equal to or larger than 600 mV, and the rate of hydrogen evolution becomes larger (hydrogen is readier to evolve) with reduction of the flow rate of air.

[0053] Relation of the running voltage with the current density applied is shown in Fig. 4.

The areas in Fig. 2 where the efficiency of hydrogen evolution is 100% or more fall below the line defined by the running voltage being equal to or lower than 600 mV in Fig. 4.

[0054] Relation of the energy efficiency with the running voltage (applied voltage) is shown in Fig. 5.

From this it was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV, and the energy efficiency is particularly high when the running voltage is kept equal to or smaller than 600 mV, and the flow of air is kept at 30 to 50 ml/min.

[0055] Next, the cell was operated under a condition of temperature at 50°C; rate of fuel flow at 5 ml/min; rate of air flow at 50 ml/min; and current density at 4.8 mA/cm^2 to cause gas to evolve. The concentration of hydrogen in the

gas was determined by gas chromatography. As a result it was found that the gas contained hydrogen at about 86%, and hydrogen evolved at a rate of 7.8 ml/min. No CO was detected.

【Example 2】

[0056] The same hydrogen generating cell as that of hydrogen generation example 1 was used. The cell was operated while the temperature being kept at 30°C with the flow of air to the air electrode varied from 10 to 70 ml/min and the flow of 1M aqueous solution of methanol (fuel) to the fuel electrode kept at 5 ml/min. Then, while the current flowing between the air electrode and the fuel electrode being varied by means of a DC power source from outside, the running voltage between the fuel electrode and the air electrode, the rate of hydrogen evolution occurring from the fuel electrode, and the energy efficiency were monitored and analyzed.

[0057] In this test, relation of the rate of hydrogen evolution with the current density applied is shown in Fig. 6, relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 7, and relation of the running voltage with the current density is shown in Fig. 8.

From this it was found that the volume of hydrogen evolution tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 400 mV; hydrogen is readier to evolve with reduction of the flow rate of air; and the rate of hydrogen

evolution becomes virtually constant with the air flow of 10 ml/min, when the running voltage becomes equal to or larger than 600 mV, while the rate of hydrogen evolution tends to grow with the air flow of 30 ml/min, when the running voltage becomes equal to or larger than 800 mV, and thus no hydrogen will evolve when air flows at a higher rate unless the running voltage is raised sufficiently high.

[0058] Relation of the energy efficiency with the running voltage (applied voltage) is shown in Fig. 9.

From this it was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV, and the energy efficiency is particularly high with the air flow of 30 ml/min when the running voltage is kept equal to or smaller than 600 mV.

【Example 3】

[0059] The test was performed under the same condition as in hydrogen generation example 2 except that the temperature of the cell was kept at 70°C. The running voltage between the fuel electrode and the air electrode, and rate of hydrogen evolution on the fuel electrode and energy efficiency were monitored and analyzed.

[0060] Relation of the rate of hydrogen evolution with the current density applied during the test is shown in Fig. 10, relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 11, relation of the running voltage with the current density is shown in Fig. 12.

From this it was found that the volume of hydrogen

evolution tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 400 mV; hydrogen is readier to evolve with reduction of the flow rate of air; and the rate of hydrogen evolution becomes virtually constant with the air flow of 10 ml/min, when the running voltage becomes equal to or larger than 600 mV, while the rate of hydrogen evolution tends to grow with the air flow of 30 ml/min, when the running voltage becomes equal to or larger than 800 mV, and thus no hydrogen will evolve when air flows at a higher rate unless the running voltage is raised sufficiently high.

[0061] Relation of the energy efficiency with the running voltage is shown in Fig. 13.

It was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV, and the energy efficiency is particularly high with the flow rate of air of 10 to 30 ml/min when the running voltage is kept equal to or smaller than 600 mV.

【Example 4】

[0062] The same hydrogen generating cell as that of hydrogen generation example 1 was used. The cell was operated while the temperature being kept at 90°C with the flow rate of air to the air electrode varied from 10 to 200 ml/min and the flow of 1M aqueous solution of methanol (fuel) to the fuel electrode kept at 5 ml/min. Then, while the current flowing between the air electrode and the fuel electrode being varied by means of a DC power source from

outside, the running voltage between the fuel electrode and the air electrode, the rate of hydrogen evolution occurring from the fuel electrode, and the energy efficiency were monitored and analyzed.

[0063] Relation of the rate of hydrogen evolution with the current density applied is shown in Fig. 14, and relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 15, and relation of the running voltage with the current density is shown in Fig. 16.

From this it was found that the volume of hydrogen evolution tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 300 mV; hydrogen is readier to evolve with reduction of the flow rate of air; and the rate of hydrogen evolution becomes virtually constant with the air flow of 10 ml/min, when the running voltage becomes equal to or larger than 500 mV, while the rate of hydrogen evolution tends to grow with the air flow of 50 to 100 ml/min, when the running voltage becomes equal to or larger than 800 mV, and thus no hydrogen will evolve when air flows at 200 ml/min unless the running voltage is raised higher than 800 mV.

[0064] Relation of the energy efficiency with the running voltage (applied voltage) is shown in Fig. 17.

From this it was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV, and the energy efficiency is

particularly high with the flow of air of 50 ml/min when the running voltage is kept equal to or smaller than 500 mV.

[0065] Next, for examples 1 to 4 where operation temperature was varied with the flow of air kept at 50 ml/min, relation of the rate of hydrogen evolution with the current density applied is shown in Fig. 18, while relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 19, and relation of the running voltage with the current density is shown in Fig. 20.

From this it was found that the rate of hydrogen evolution tends to depend on the temperature: hydrogen evolves at a low running voltage and the rate of hydrogen evolution becomes higher as the temperature is raised.

[0066] Relation of the energy efficiency with the running voltage (applied voltage) is shown in Fig. 21.

It was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV, and the energy efficiency is particularly high when the running voltage is kept equal to or smaller than 600 mV.

【Example 5】

[0067] The same hydrogen generating cell with that of example 1 was used. The cell was operated while the temperature being kept at 50°C with the flow of air to the air electrode kept at 50 ml/min and the flow of fuel to the fuel electrode varied to 1.5, 2.5, 5.0, 7.5, or 10.0 ml/min. Then, while the current flowing between the air electrode

and the fuel electrode being varied by means of a DC power source from outside, the running voltage between the fuel electrode and the air electrode, the rate of hydrogen evolution occurring from the fuel electrode, and the energy efficiency were monitored and analyzed.

[0068] Relation of the rate of hydrogen evolution with the current density applied is shown in Fig. 22, relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 23, and relation of the running voltage with the current density is shown in Fig. 24.

It was found that the volume of hydrogen evolution tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 400 mV; hydrogen is readier to evolve with increase of the flow rate of fuel; and the rate of hydrogen evolution tends to grow when the running voltage is equal to or larger than 800 mV for all the flow rates of fuel tested.

[0069] Relation of the energy efficiency with the running voltage (applied voltage) is shown in Fig. 25.

It was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV, and the energy efficiency is particularly high when the running voltage is kept equal to or smaller than 600 mV in any case of the rate of fuel flow.

【Example 6】

[0070] The same hydrogen generating cell as that of example 1 was used. The cell was operated while the

temperature being kept at 50°C with the flow of air to the air electrode kept at 50 ml/min and the constant flow of fuel to the fuel electrode kept at 5 ml/min while fuel concentration being varied to 0.5, 1, 2, or 3M. Then, while the external current flowing between the air electrode and the fuel electrode being varied by means of a DC power source from outside, the running voltage between the fuel electrode and the air electrode, the rate of hydrogen evolution occurring from the fuel electrode, and the energy efficiency were monitored and analyzed.

[0071] Relation of the rate of hydrogen evolution with the current density applied is shown in Fig. 26, relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 27, and relation of the running voltage with the current density is shown in Fig. 28.

From this it was found that the rate of hydrogen evolution grows almost linearly with the increase of current density provided that the current density is equal to or higher than $0.02A/cm^2$ in any case of the concentration of fuel.

It was also found that the volume of hydrogen evolution tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 400 mV; hydrogen is readier to evolve with increase of the concentration of fuel, and the rate of hydrogen evolution grows sharply under the fuel concentration of 2M or 3M, when the running voltage

approaches 400 to 500 mV; and the rate of hydrogen evolution becomes virtually constant under the fuel concentration of 1M when the running voltage is in the range of 400 to 800 mV, while the rate of hydrogen evolution tends to grow when the running voltage becomes equal to or larger than 800 mV, and no hydrogen will evolve when the fuel concentration is lower than this level (1M) unless the running voltage is raised sufficiently high.

[0072] Relation of the energy efficiency with the running voltage is shown in Fig. 29.

It was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV except for a case where the fuel concentration is kept at 0.5M, and the energy efficiency is particularly high with the concentration of the fuel being 1, 2 or 3M when the running voltage is kept equal to or smaller than 600 mV. When the concentration of fuel was 0.5M, no hydrogen evolved when the running voltage was low. Under this condition, the cell behaved quite differently in terms of energy efficiency.

【Example 7】

[0073] The same hydrogen generating cell with that of example 1 was used. The cell was operated while the temperature being kept at 50°C with the constant flow of 1M fuel to the fuel electrode kept at 5 ml/min and the flow of oxidizing gas to the oxidizing electrode kept at 14.0 ml/min while oxygen concentration being varied to 10, 21,

40, or 100%. Then, while the current flowing between the oxidizing electrode and the fuel electrode being varied by means of a DC power source from outside, the running voltage between the fuel electrode and the oxidizing electrode, the rate of hydrogen evolution occurring from the fuel electrode, and the energy efficiency were monitored and analyzed. The oxidizing gas containing 21% oxygen was represented by air, and the oxidizing gas containing 10% oxygen was obtained by mixing air with nitrogen. The oxidizing gas containing 40% oxygen was obtained by adding oxygen (100% oxygen) to air.

[0074] Relation of the rate of hydrogen evolution with the current density applied is shown in Fig. 30, relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 31, relation of the running voltage with the current density is shown in Fig. 32.

From this it was found that the volume of hydrogen evolution grows almost linearly with the increase of current density provided that the current density is equal to or higher than 0.03 A/cm^2 in any case of the concentration of oxygen.

It was also found that the volume of hydrogen evolution tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 400 mV; hydrogen is readier to evolve with increase of the concentration of oxygen; and the rate of hydrogen evolution becomes virtually constant under when

the running voltage is in the range of 400 to 800 mV, while it tends to grow when the running voltage becomes equal to or larger than 800 mV.

[0075] Relation of the energy efficiency with the running voltage is shown in Fig. 33.

It was found that the energy efficiency is equal to or larger than 100% even when the applied voltage is around 1000 mV, and the energy efficiency is particularly high with the concentration of oxygen being high when the applied voltage is kept equal to or smaller than 600 mV.

【Example 8】

[0076] The same hydrogen generating cell as that of example 1 was used (except that the air electrode consisted of an oxidizing electrode to which liquid was flowed). The hydrogen generating cell was placed in an electric furnace where hot air was circulated. The cell was operated while the temperature being varied to 30, 50, 70, or 90°C with the flow of 1M aqueous solution of methanol to the fuel electrode kept at 5 ml/min and the flow of 1M H_2O_2 (hydrogen peroxide) to the oxidizing electrode varied from 2.6 to 5.5 ml/min,. Then, while the current flowing between the oxidizing electrode and the fuel electrode being varied by means of a DC power source from outside, the running voltage between the fuel electrode and the oxidizing electrode, the rate of hydrogen evolution occurring from the fuel electrode, and the energy efficiency were monitored and analyzed.

The flow rate of hydrogen peroxide was adjusted such that the open-circuit voltage was approximately equal to 500 mV for all the temperatures tested.

[0077] Relation of the rate of hydrogen evolution with the current density applied is shown in Fig. 34, relation of the rate of hydrogen evolution with the running voltage is shown in Fig. 35, and relation of the running voltage with the current density is shown in Fig. 36.

From this it was found that the volume of hydrogen evolution tends to depend on the running voltage, and hydrogen evolves when the running voltage is equal to or larger than 500 mV, and tends to grow when the running voltage is equal to or larger than 800 mV; and hydrogen is readier to evolve with increase of the operation temperature.

[0078] Relation of the energy efficiency with the running voltage is shown in Fig. 37.

It was found that the energy efficiency is equal to or larger than 100% even when the running voltage is around 1000 mV, and the energy efficiency is particularly high with the temperature of 90°C when the running voltage is kept equal to or smaller than 800 mV.

[0079] What is important here is that hydrogen was withdrawn from the hydrogen generating cells of Examples whose energy content exceeded the electric current supplied from outside. In other words, the hydrogen generating cell of the invention generates more hydrogen than is explained

by the consumption of supplied electric energy. In addition, conversion of fuel into hydrogen occurred at a surprisingly low temperature of 30 to 90°C. In view of these facts, the hydrogen generating method of the invention and hydrogen generating system based on the method are likely to be novel ones that have never been observed before.

【BRIEF DESCRIPTION OF THE DRAWINGS】

[0080] Fig. 1 is a schematic diagram of a hydrogen generating cell described in Example.

Fig. 2 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with the current density applied when the flow rate of air is varied.

Fig. 3 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with the running voltage when the flow rate of air is varied.

Fig. 4 shows a graph for indicating relation of the running voltage (temperature at 50°C) with the current density applied when the flow rate of air is varied.

Fig. 5 shows a graph for indicating relation of the energy efficiency (temperature at 50°C) with the running voltage when the flow rate of air is varied.

Fig. 6 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 30°C) with the current density applied when the flow rate of air is varied.

Fig. 7 shows a graph for indicating relation of the

rate of hydrogen evolution (temperature at 30°C) with the running voltage when the flow rate of air is varied.

Fig. 8 shows a graph for indicating relation of the running voltage (temperature at 30°C) with the current density applied when the flow rate of air is varied.

Fig. 9 shows a graph for indicating relation of the energy efficiency (temperature at 30°C) with the running voltage when the flow rate of air is varied.

Fig. 10 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 70°C) with the current density applied when the flow rate of air is varied.

Fig. 11 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 70°C) with the running voltage when the flow rate of air is varied.

Fig. 12 shows a graph for indicating relation of the running voltage (temperature at 70°C) with the current density applied when the flow rate of air is varied.

Fig. 13 shows a graph for indicating relation of the energy efficiency (temperature at 70°C) with the running voltage when the flow rate of air is varied.

Fig. 14 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 90°C) with the current density applied when the flow rate of air is varied.

Fig. 15 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 90°C) with

the running voltage when the flow rate of air is varied.

Fig. 16 shows a graph for indicating relation of the running voltage (temperature at 90°C) with the current density applied when the flow rate of air is varied.

Fig. 17 shows a graph for indicating relation of the energy efficiency (temperature at 90°C) with the running voltage when the flow rate of air is varied.

Fig. 18 shows a graph for indicating relation of the rate of hydrogen evolution (flow rate of air at 50 ml/min) with the current density applied when the temperature is varied.

Fig. 19 shows a graph for indicating relation of the rate of hydrogen evolution (flow rate of air at 50 ml/min) with the running voltage when the temperature is varied.

Fig. 20 shows a graph for indicating relation of the running voltage (flow rate of air at 50 ml/min) with the current density applied when the temperature is varied.

Fig. 21 shows a graph for indicating relation of the energy efficiency (flow rate of air at 50 ml/min) with the running voltage when the temperature is varied.

Fig. 22 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with the current density applied when the flow rate of fuel is varied.

Fig. 23 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with

the running voltage when the flow rate of fuel is varied.

Fig. 24 shows a graph for indicating relation of the running voltage (temperature at 50°C) with the current density applied when the flow rate of fuel is varied.

Fig. 25 shows a graph for indicating relation of the energy efficiency (temperature at 50°C) with the running voltage when the flow rate of fuel is varied.

Fig. 26 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with the current density applied when the concentration of fuel is varied.

Fig. 27 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with the running voltage when the concentration of fuel is varied.

Fig. 28 shows a graph for indicating relation of the running voltage (temperature at 50°C) with the current density applied when the concentration of fuel is varied.

Fig. 29 shows a graph for indicating relation of the energy efficiency (temperature at 50°C) with the running voltage when the concentration of fuel is varied.

Fig. 30 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with the current density applied when the concentration of oxygen is varied (hydrogen generating example 3-7).

Fig. 31 shows a graph for indicating relation of the rate of hydrogen evolution (temperature at 50°C) with

the running voltage when the concentration of oxygen is varied.

Fig. 32 shows a graph for indicating relation of the running voltage (temperature at 50°C) with the current density applied when the concentration of oxygen is varied.

Fig. 33 shows a graph for indicating relation of the energy efficiency (temperature at 50°C) with the running voltage when the concentration of oxygen is varied.

Fig. 34 shows a graph for indicating relation of the rate of hydrogen evolution (oxidizing agent of H_2O_2) with the current density applied when the temperature is varied.

Fig. 35 shows a graph for indicating relation of the rate of hydrogen evolution (oxidizing agent of H_2O_2) with the running voltage when the temperature is varied.

Fig. 36 shows a graph for indicating relation of the running voltage (oxidizing agent of H_2O_2) with the current density applied when the temperature is varied.

Fig. 37 shows a graph for indicating relation of the energy efficiency (oxidizing agent of H_2O_2) with the running voltage when the temperature is varied.

【DOCUMENT NAME】 ABSTRACT

【Abstract】

【Problems】

The present invention aims to provide a hydrogen generating method for generating hydrogen-containing gas little contaminated with nitrogen, etc., by decomposing fuel containing an organic compound at low temperature while requiring the supply of a little electric energy from an external source, and a hydrogen generating system based on the method.

【Measures】

The hydrogen generating method and hydrogen generating system based on the method comprises providing a fuel electrode in contact with one surface of a partition membrane, supplying fuel containing an organic compound and water to the fuel electrode, providing an oxidizing electrode in contact with the other surface of the partition membrane, supplying an oxidizing agent to the oxidizing electrode, and providing electric energy from outside to the hydrogen generating cell with the fuel electrode serving as cathode and the oxidizing electrode as anode, thereby fuel containing the organic compound is decomposed and hydrogen-containing gas is generated on the fuel electrode. Further, the volume of hydrogen-containing gas evolution can be adjusted by varying the running voltage (300 to 1000mV) between the fuel electrode and oxidizing electrode.

【Selected Drawing】 Figure 1

FIG. 1

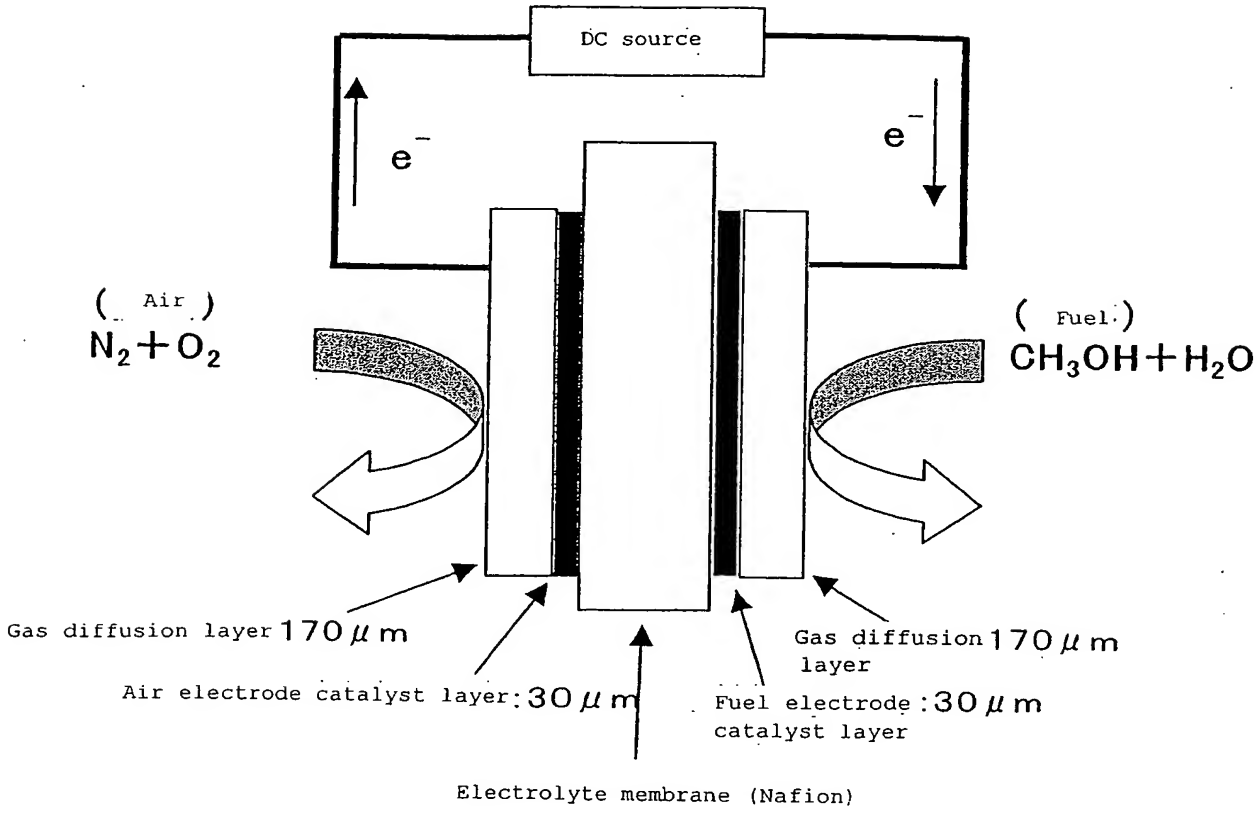

DC source
e⁻
e⁻
(Air)
N2+O2
(Fuel)
CH3OH+H2O
Gas diffusion layer 170 μm
Air electrode catalyst layer: 30 μm
Gas diffusion layer 170 μm
Fuel electrode catalyst layer: 30 μm
Electrolyte membrane (Nafion)

FIG. 2

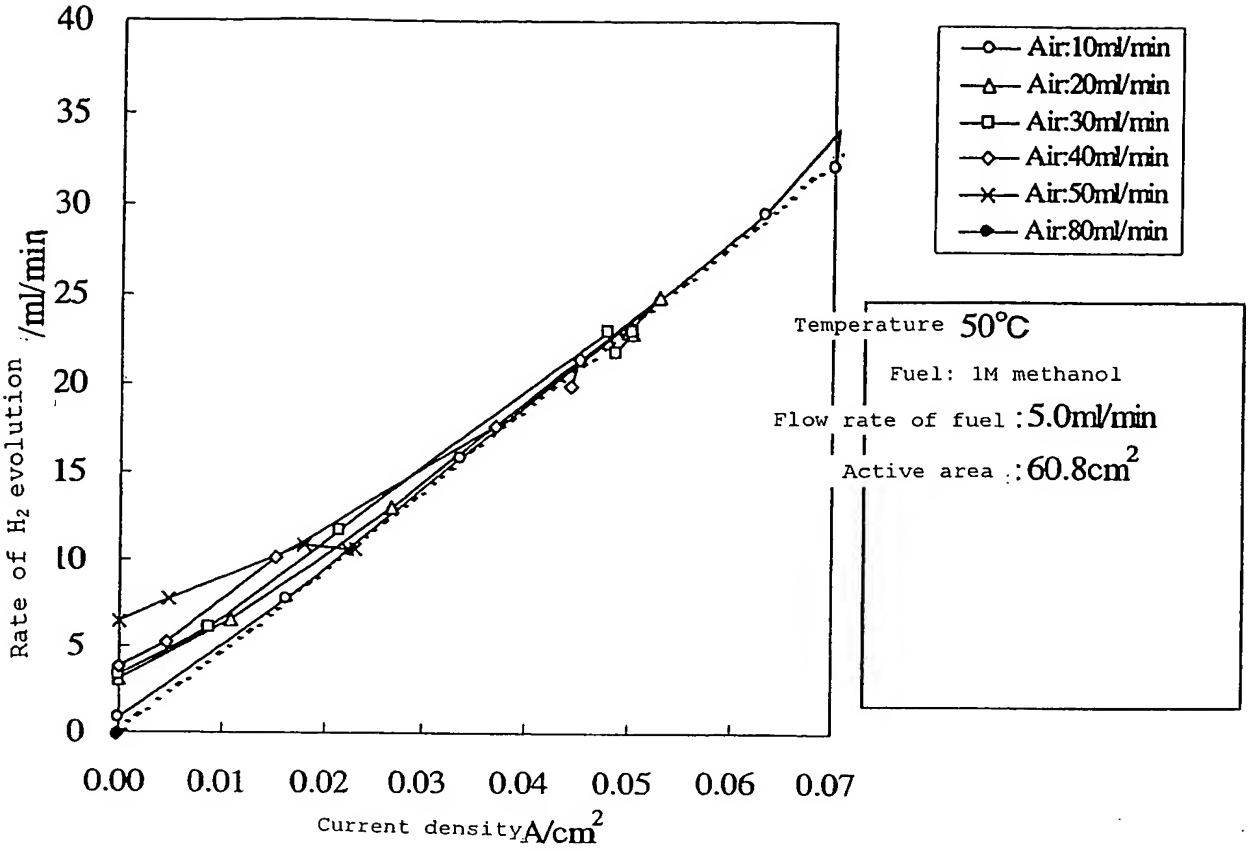

Air:10ml/min
Air:20ml/min
Air:30ml/min
Air:40ml/min
Air:50ml/min
Air:80ml/min
Temperature 50°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm2
Rate of H2 evolution /ml/min
Current density A/cm2
0
5
10
15
20
25
30
35
40
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07

FIG. 3

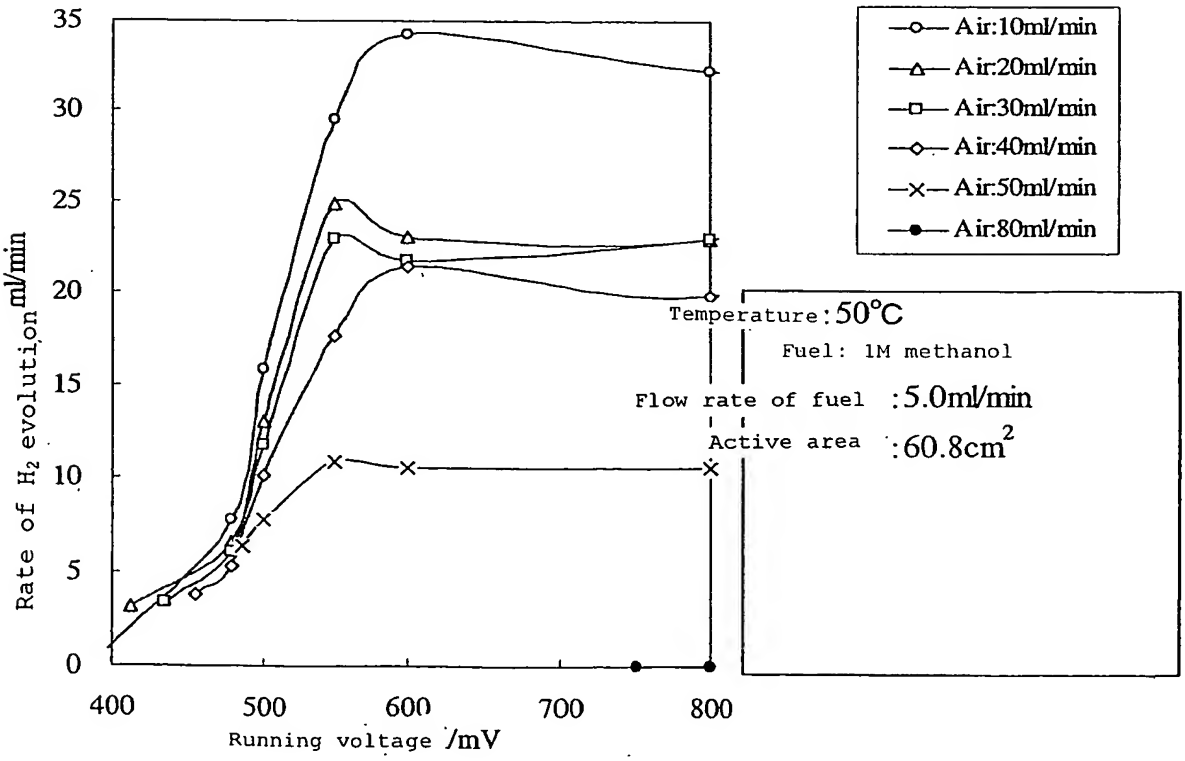

Air:10ml/min
Air:20ml/min
Air:30ml/min
Air:40ml/min
Air:50ml/min
Air:80ml/min
Temperature:50°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm2
Rate of H2 evolution ml/min
Running voltage /mV
0
5
10
15
20
25
30
35
400
500
600
700
800

FIG. 4

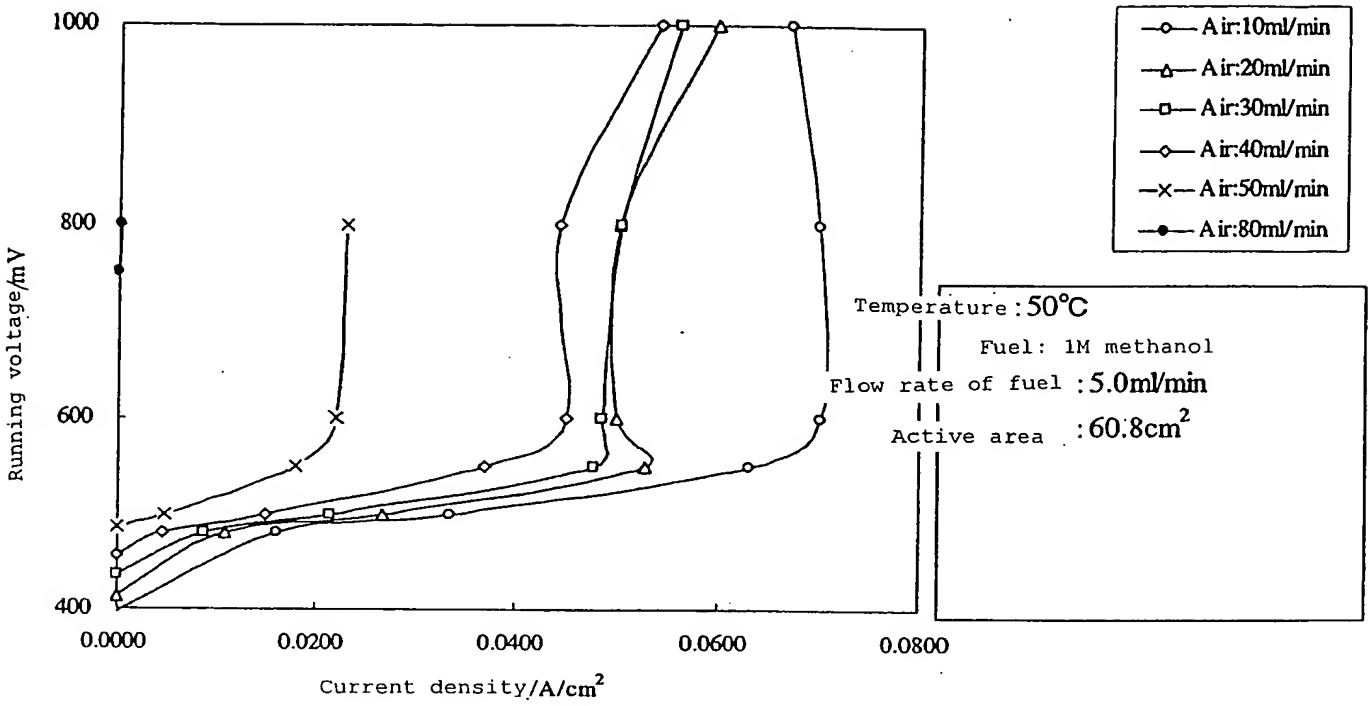

Air:10ml/min
Air:20ml/min
Air:30ml/min
Air:40ml/min
Air:50ml/min
Air:80ml/min
Temperature : 50°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Active area : 60.8cm²
Running voltage/mV
1000
800
600
400
0.0000
0.0200
0.0400
0.0600
0.0800
Current density/A/cm²

FIG. 5

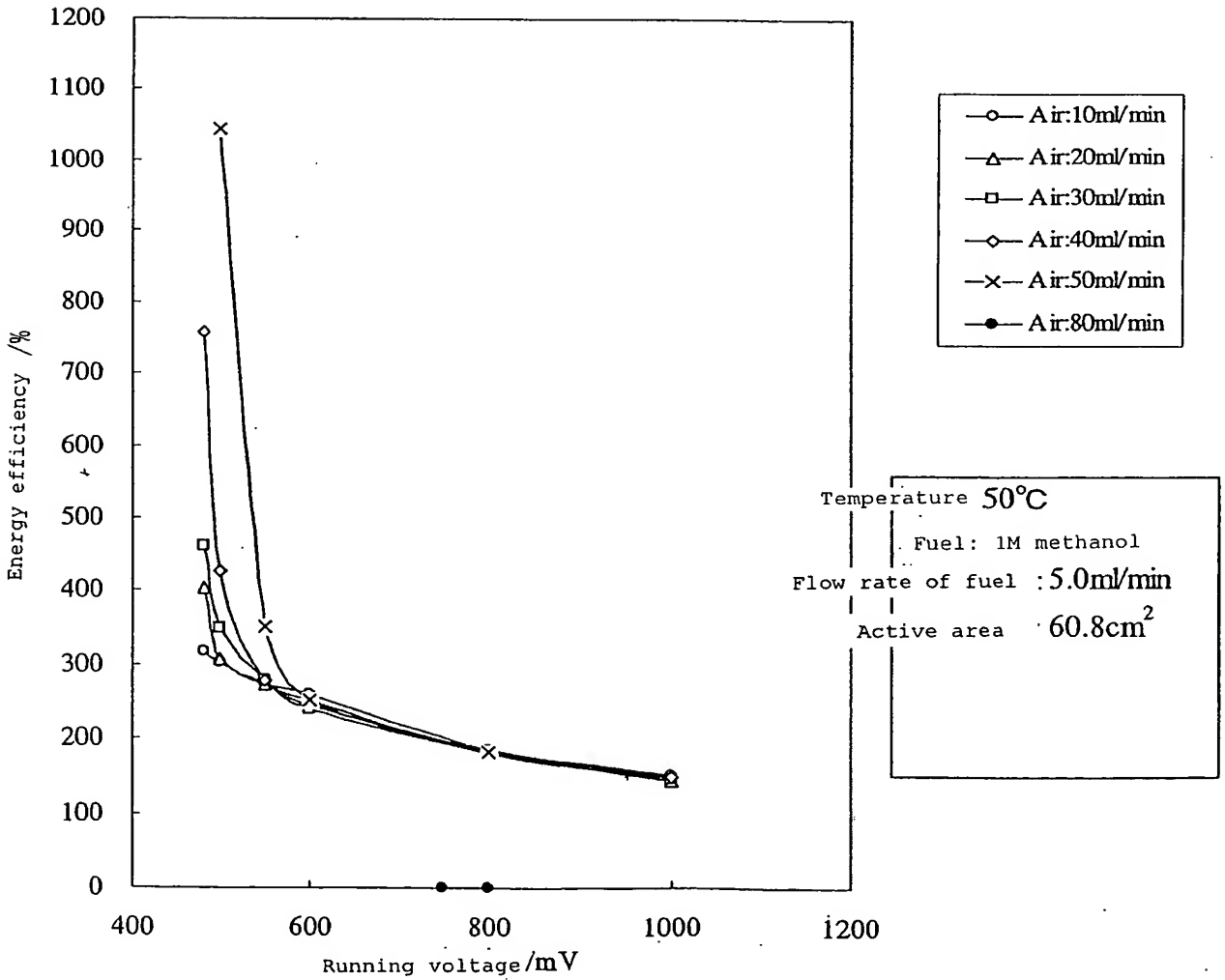

Air:10ml/min
Air:20ml/min
Air:30ml/min
Air:40ml/min
Air:50ml/min
Air:80ml/min
Temperature 50°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Active area 60.8cm²
Energy efficiency /%
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
400
600
800
1000
1200
Running voltage/mV

FIG. 6

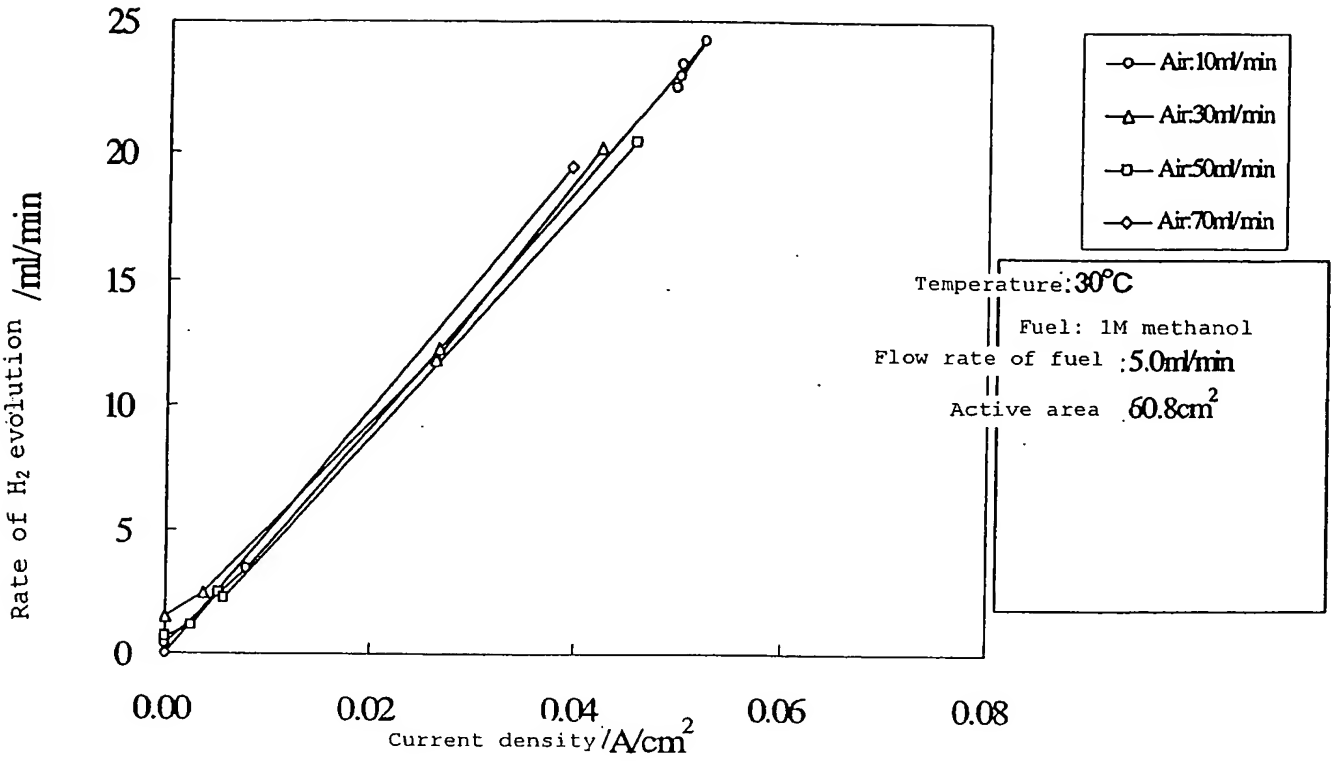

25
20
15
10
5
0
Rate of H_2 evolution /ml/min
0.00
0.02
0.04
0.06
0.08
Current density /A/cm^2
Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature:30°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area 60.8cm^2

FIG. 7

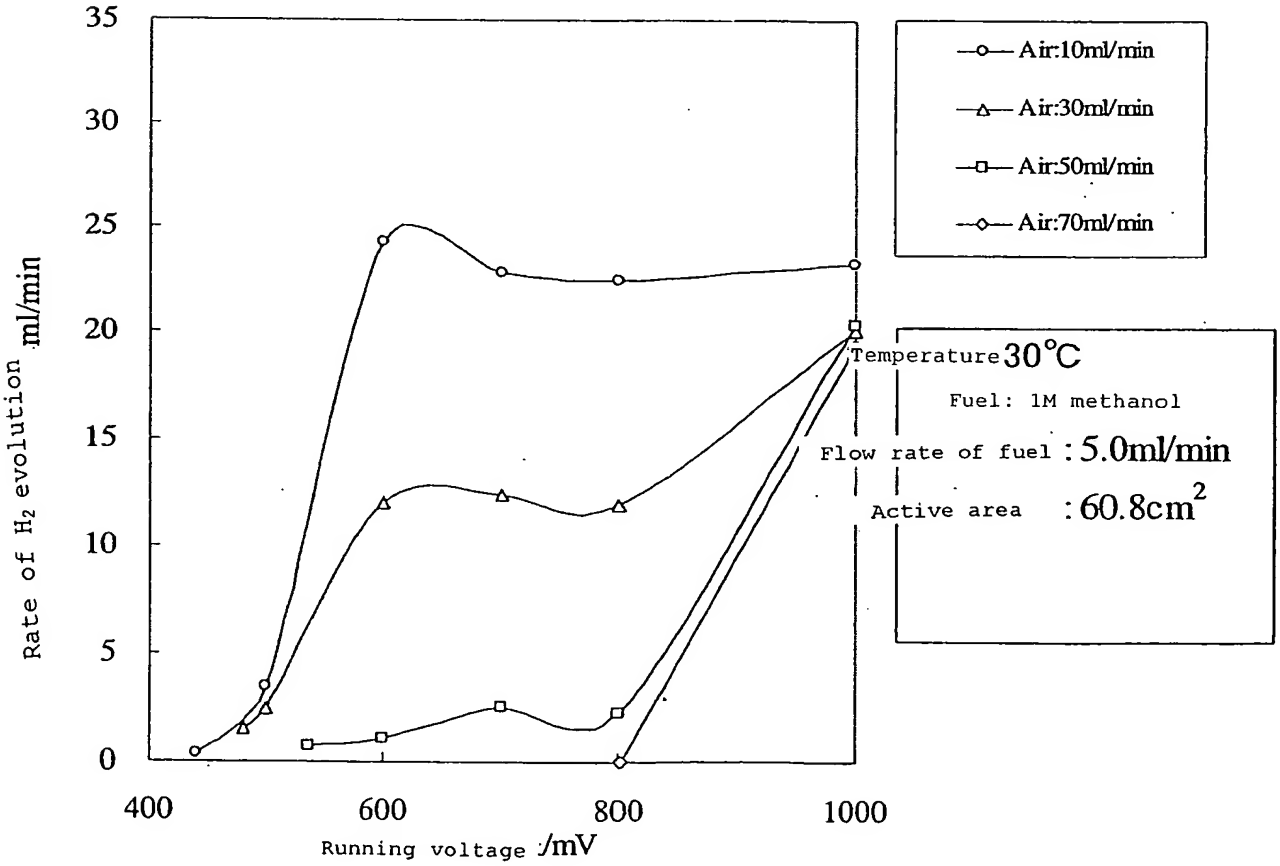

35
30
25
20
15
10
5
0
Rate of H_2 evolution ml/min
400
600
800
1000
Running voltage /mV
Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature 30°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Active area : 60.8cm^2

FIG. 8

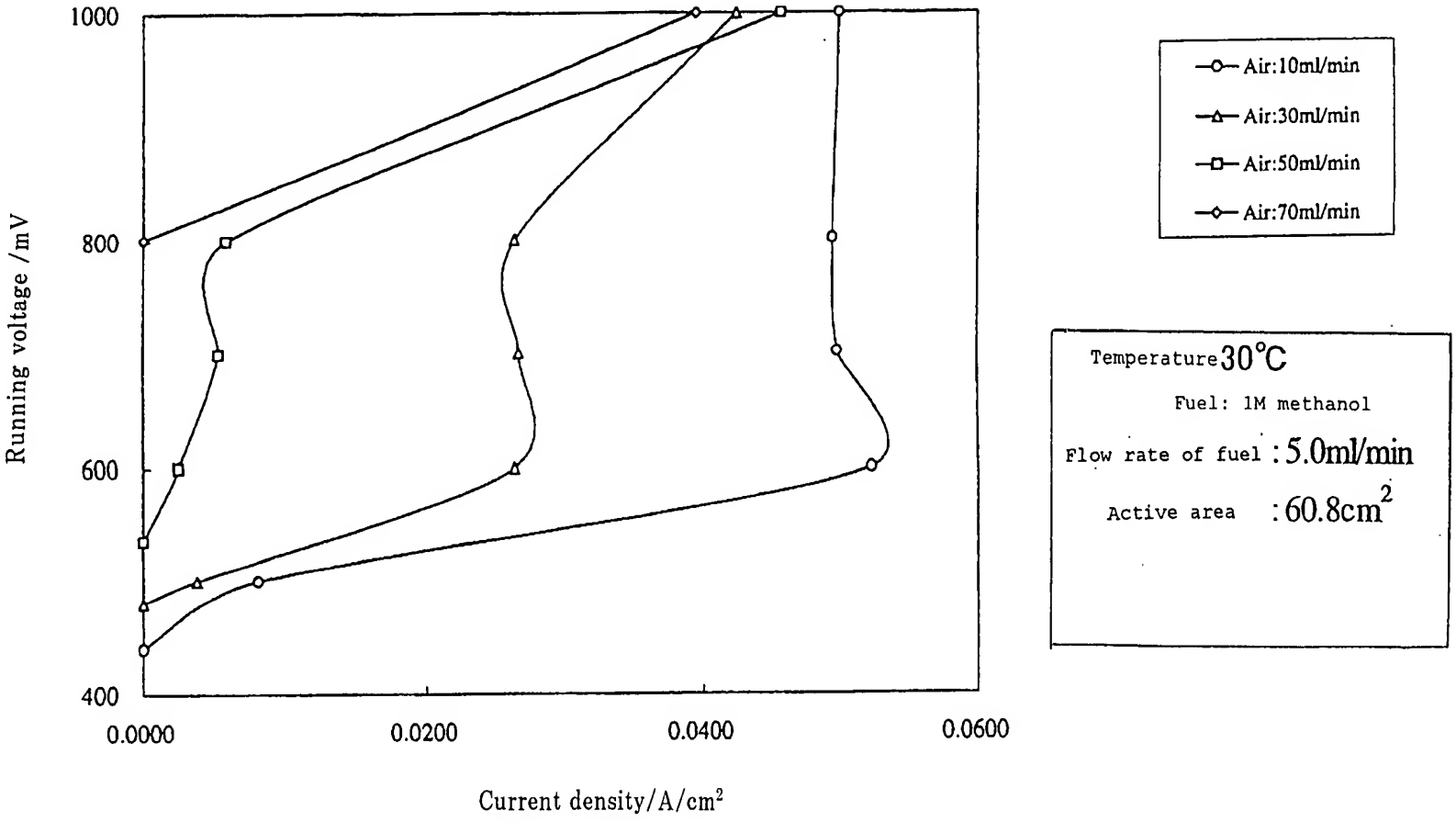

1000
800
600
400
Running voltage /mV
0.0000
0.0200
0.0400
0.0600
Current density/A/cm²
Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature 30°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Active area : 60.8cm²

FIG. 9

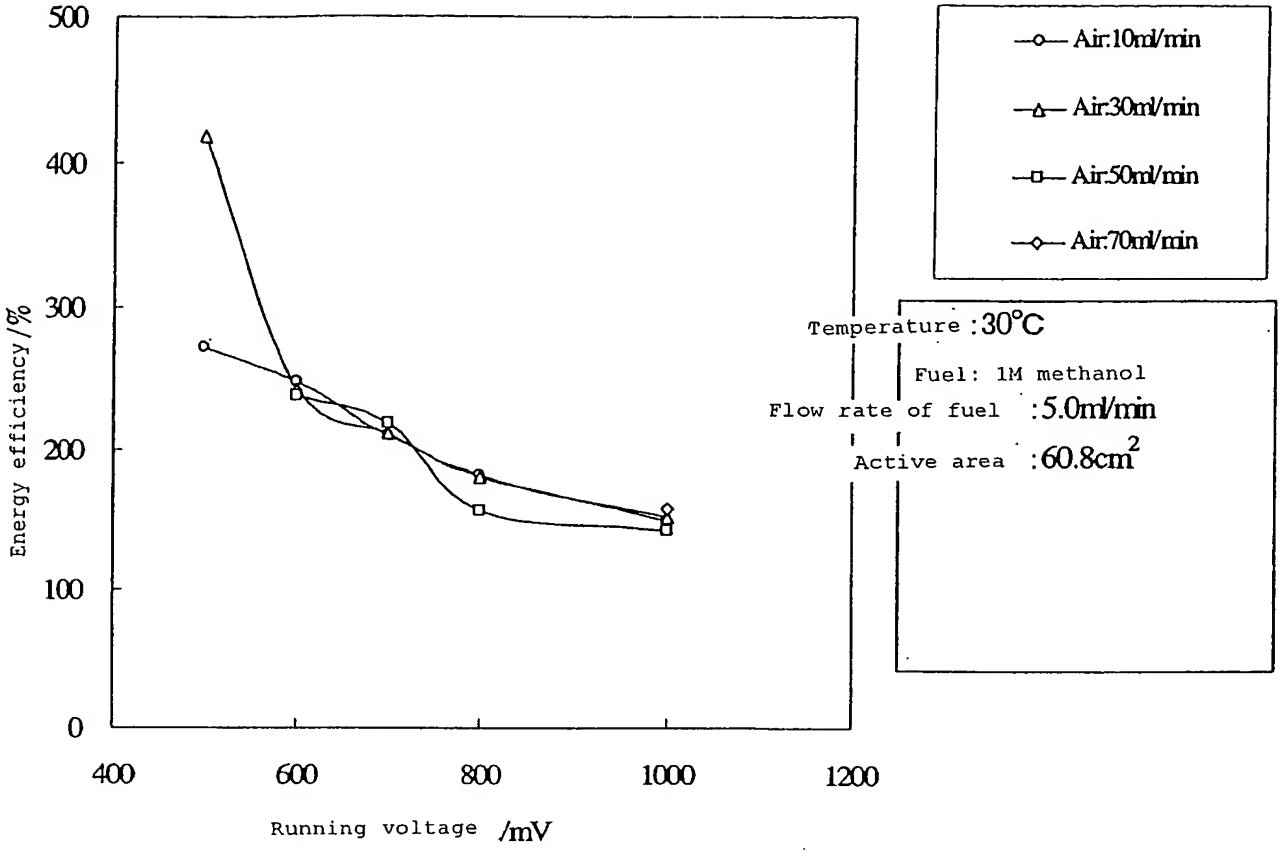

Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature :30°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm2
Energy efficiency /%
Running voltage /mV
0
100
200
300
400
500
400
600
800
1000
1200

FIG. 10

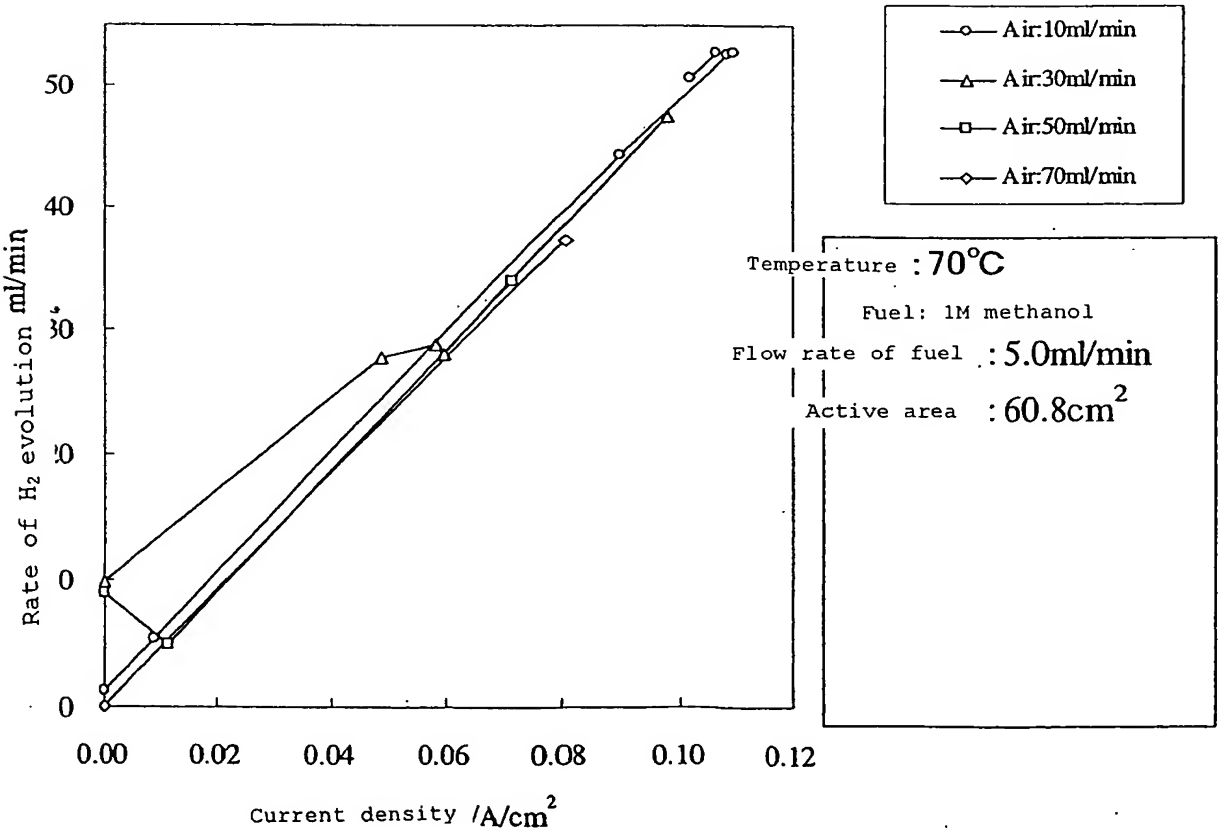

Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature :70°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm2
Rate of H2 evolution ml/min
Current density /A/cm2
0
0
40
50
0.00
0.02
0.04
0.06
0.08
0.10
0.12

FIG. 11

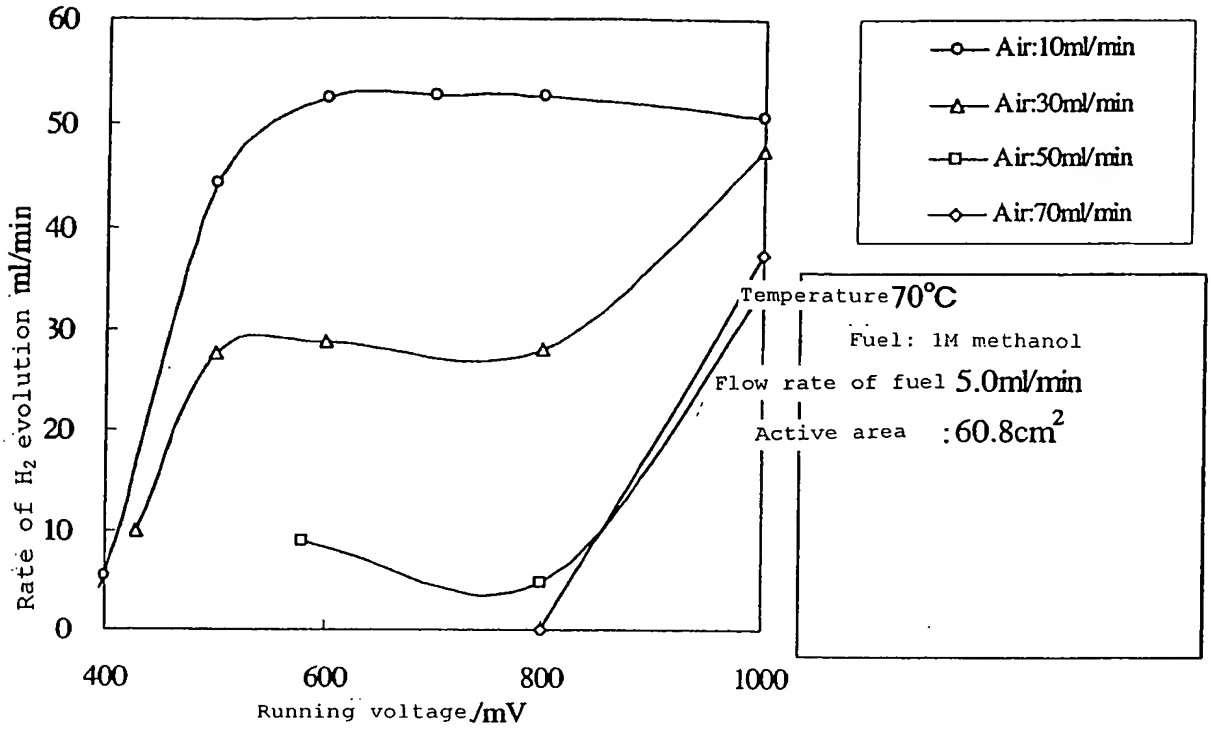

Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature 70°C
Fuel: 1M methanol
Flow rate of fuel 5.0ml/min
Active area :60.8cm2
Rate of H2 evolution ml/min
Running voltage/mV
0
10
20
30
40
50
60
400
600
800
1000

FIG. 13

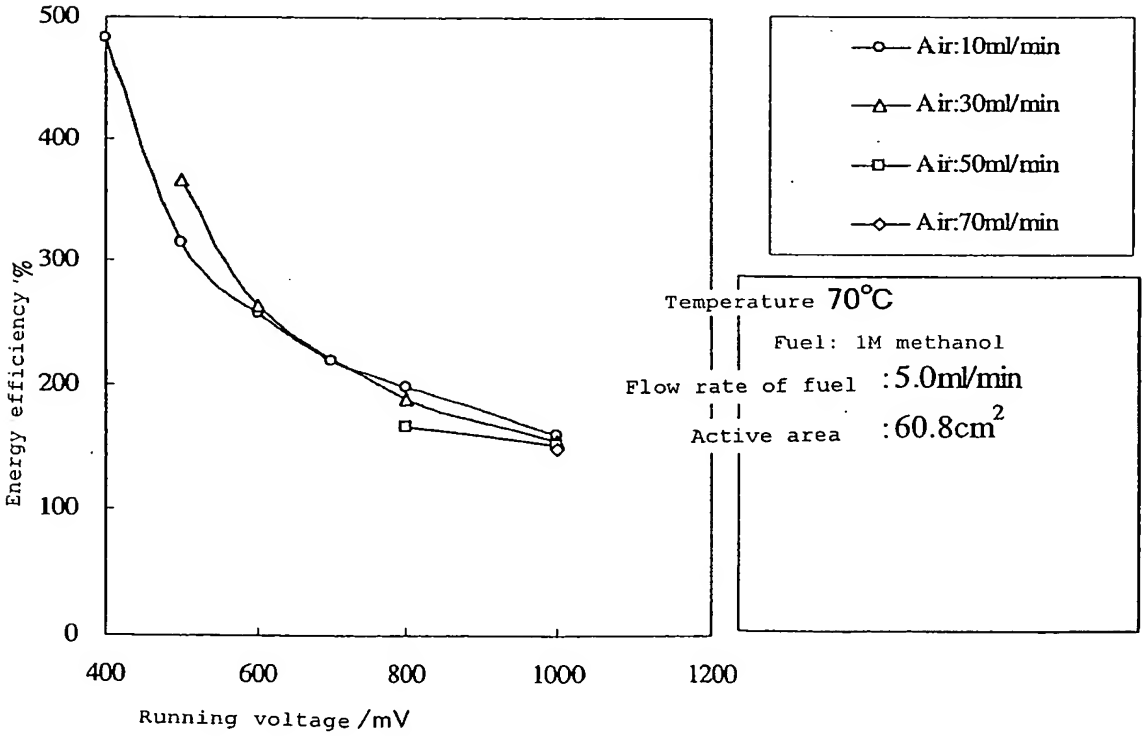

Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature 70°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm2
Energy efficiency %
Running voltage /mV
0
100
200
300
400
500
400
600
800
1000
1200

FIG. 12

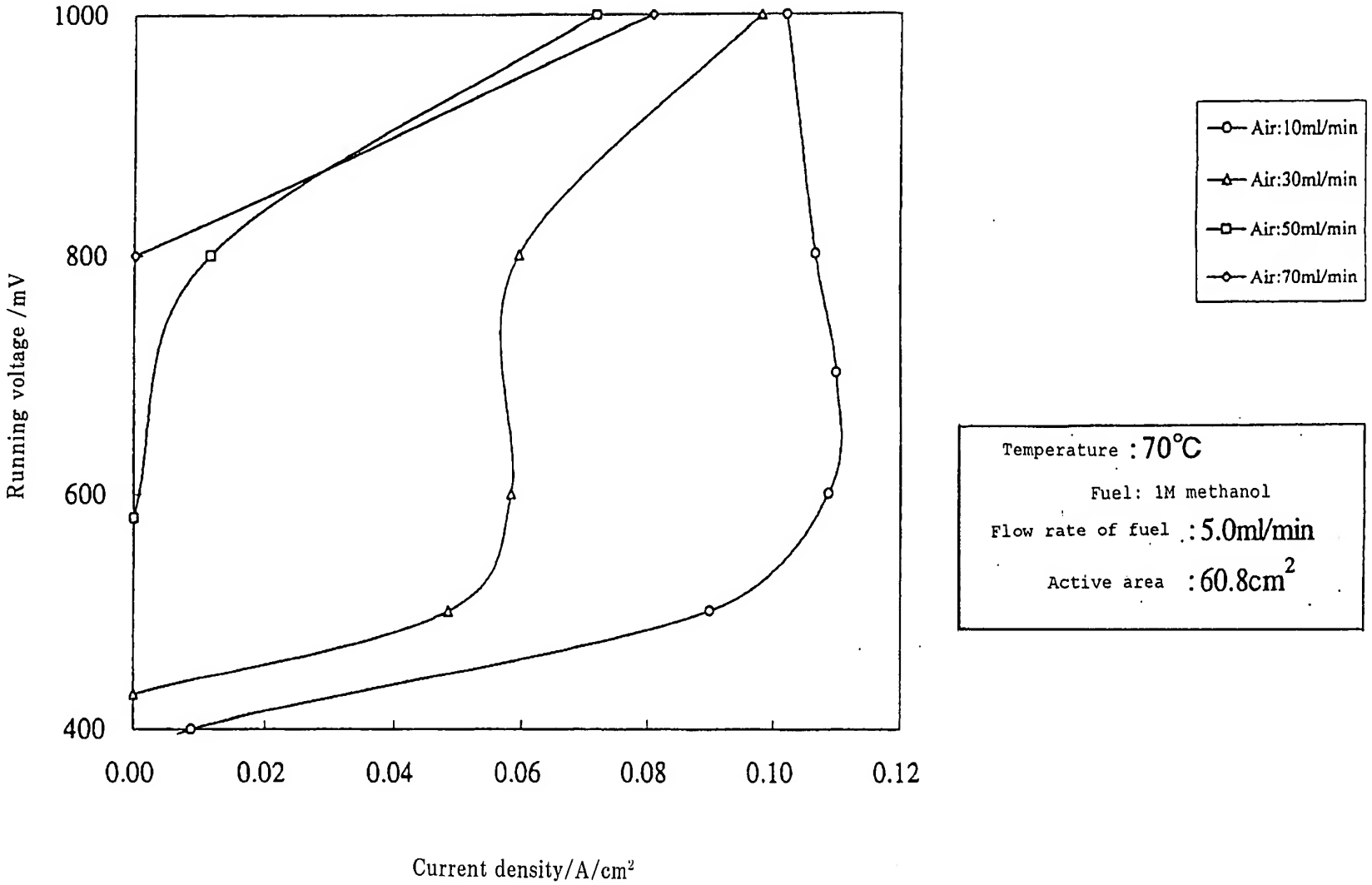

1000
800
600
400
Running voltage /mV
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Current density/A/cm²
Air:10ml/min
Air:30ml/min
Air:50ml/min
Air:70ml/min
Temperature : 70°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Active area : 60.8cm²

FIG. 14

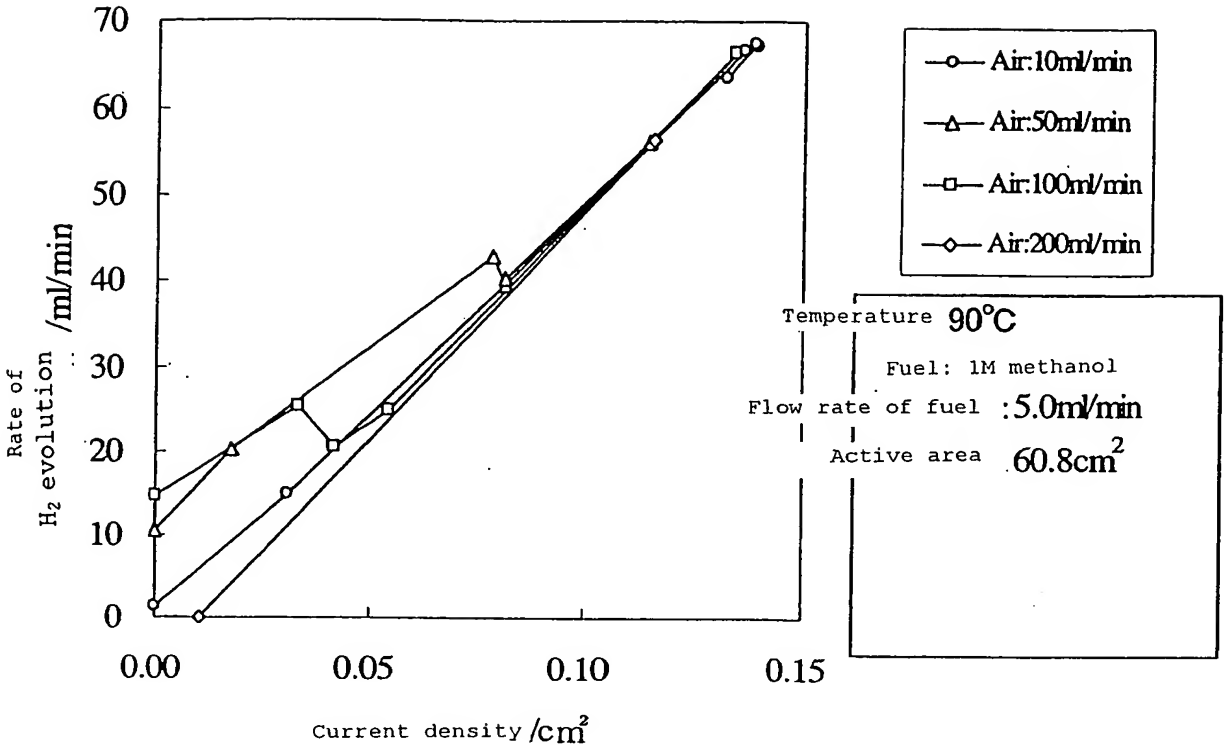

70
60
50
40
30
20
10
0
0.00
0.05
0.10
0.15
Rate of H_2 evolution /ml/min
Current density /cm^2
Air:10ml/min
Air:50ml/min
Air:100ml/min
Air:200ml/min
Temperature 90°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area 60.8cm^2

FIG. 15

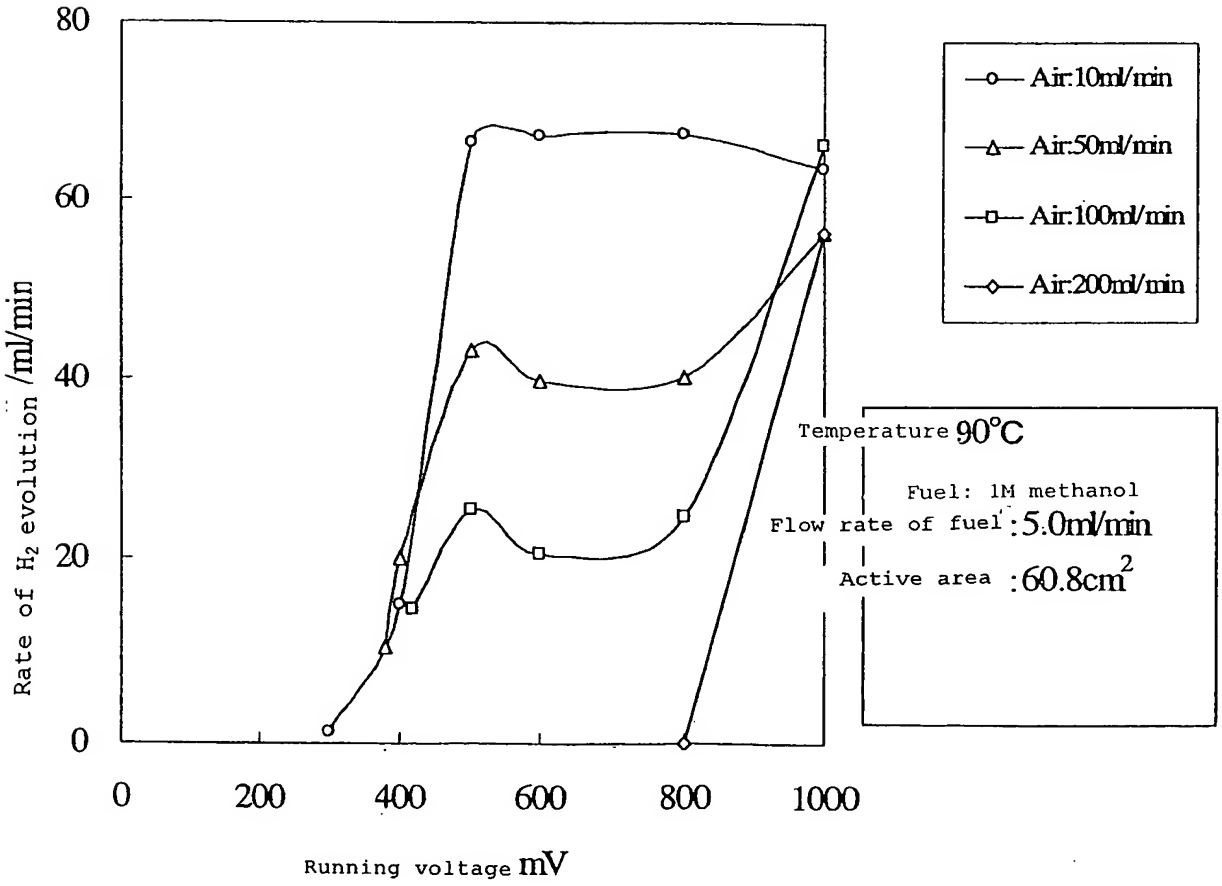

80
60
40
20
0
0
200
400
600
800
1000
Rate of H_2 evolution /ml/min
Running voltage mV
Air:10ml/min
Air:50ml/min
Air:100ml/min
Air:200ml/min
Temperature 90°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm^2

FIG. 16

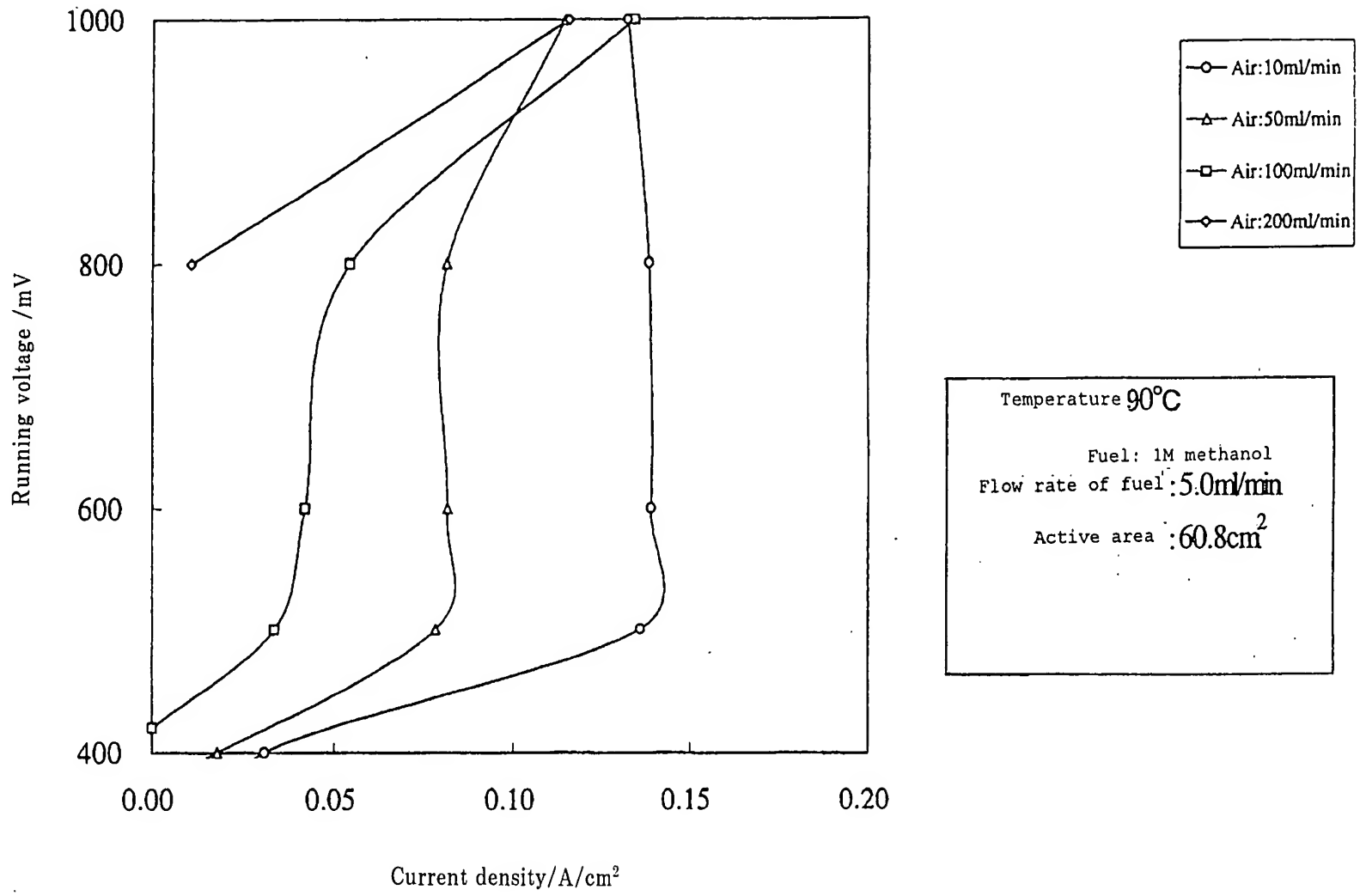

1000
800
600
400
Running voltage /mV
0.00
0.05
0.10
0.15
0.20
Current density/A/cm²
Air:10ml/min
Air:50ml/min
Air:100ml/min
Air:200ml/min
Temperature 90°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm²

FIG. 17

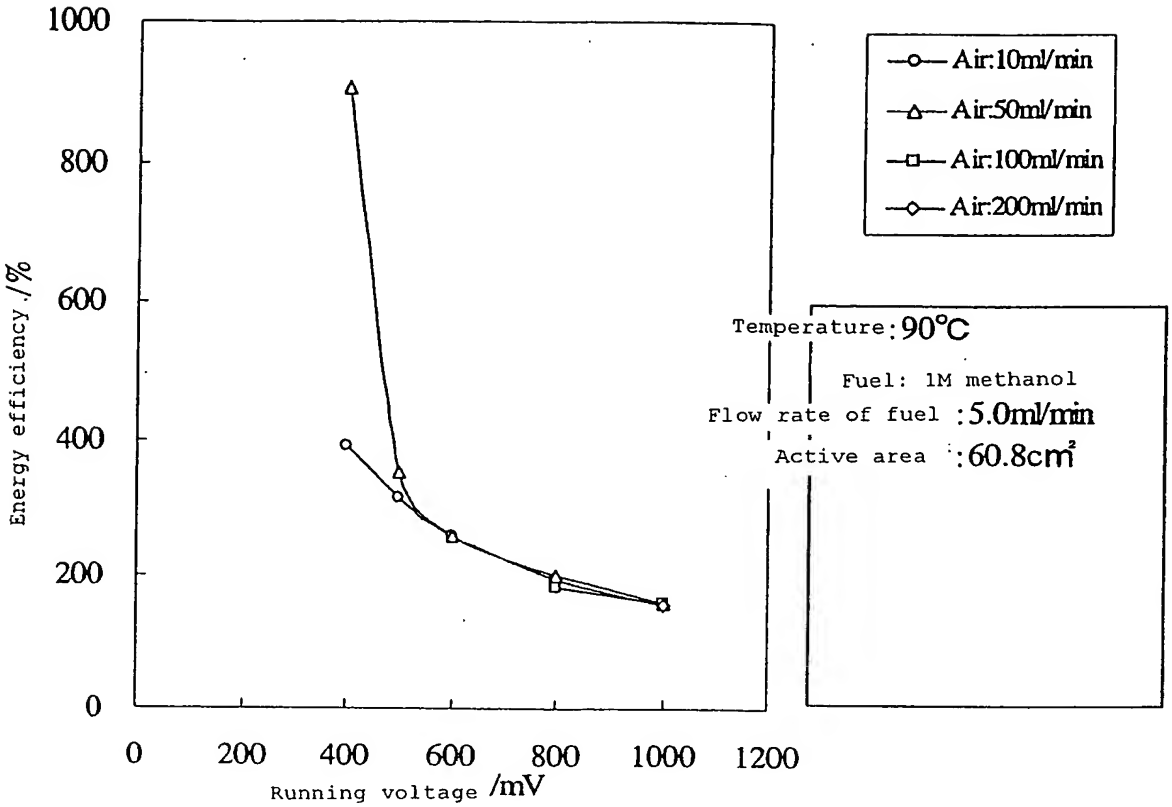

Energy efficiency /%
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
Running voltage /mV
Air:10ml/min
Air:50ml/min
Air:100ml/min
Air:200ml/min
Temperature: 90°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Active area : 60.8cm²

FIG. 18

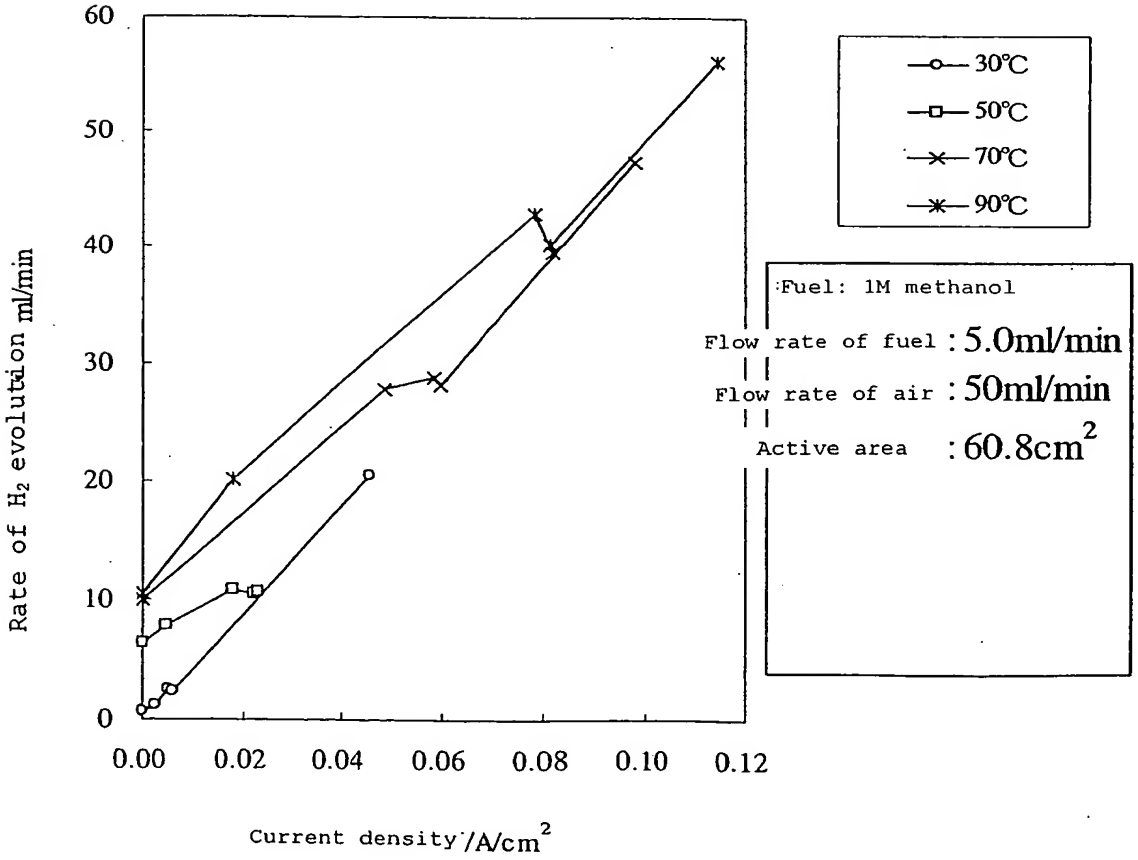

Rate of H2 evolution ml/min
60
50
40
30
20
10
0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Current density /A/cm²
30°C
50°C
70°C
90°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of air : 50ml/min
Active area : 60.8cm²

FIG. 20

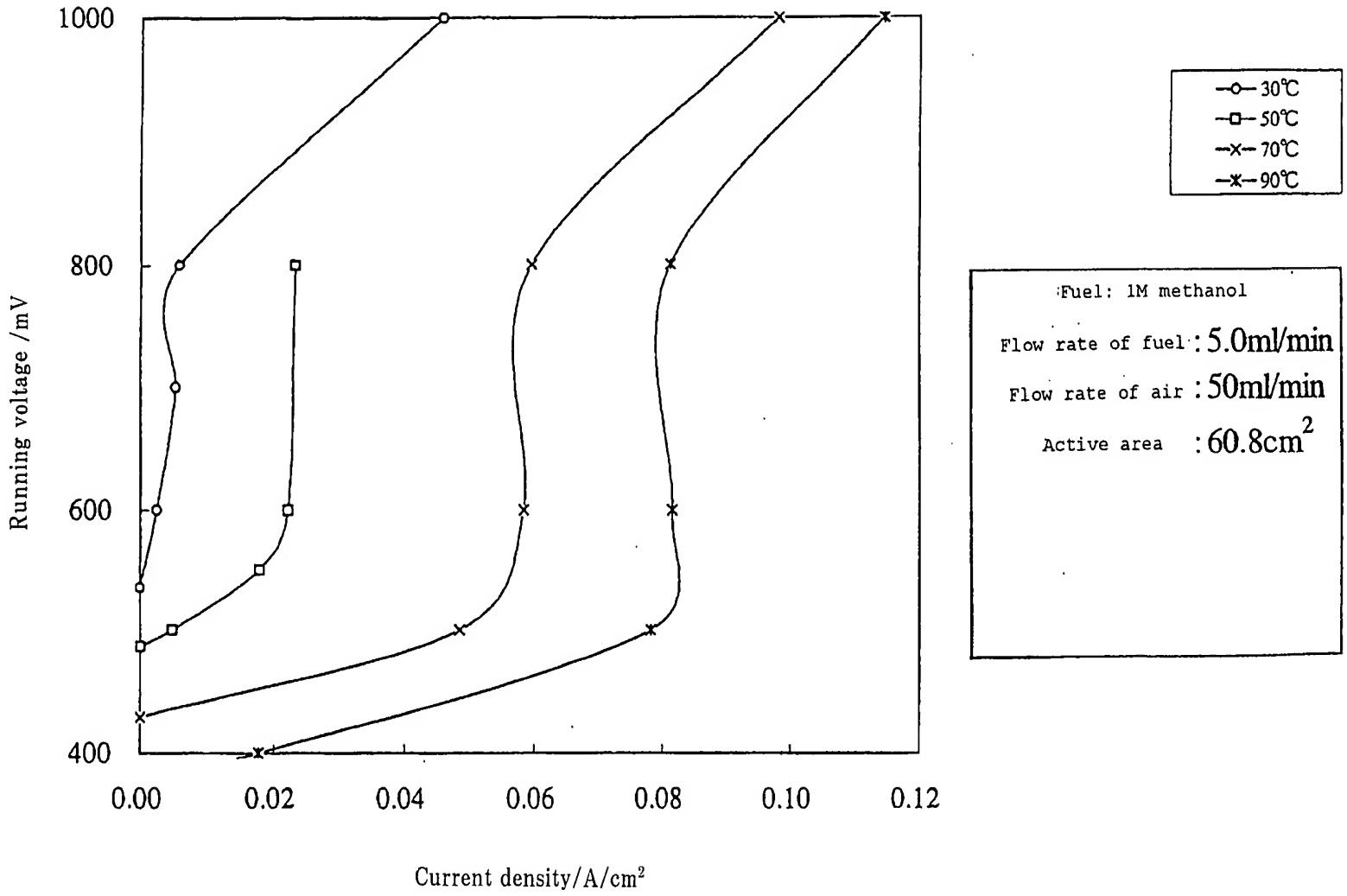

1000
800
600
400
Running voltage /mV
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Current density/A/cm²
30℃
50℃
70℃
90℃
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of air : 50ml/min
Active area : 60.8cm²

FIG. 19

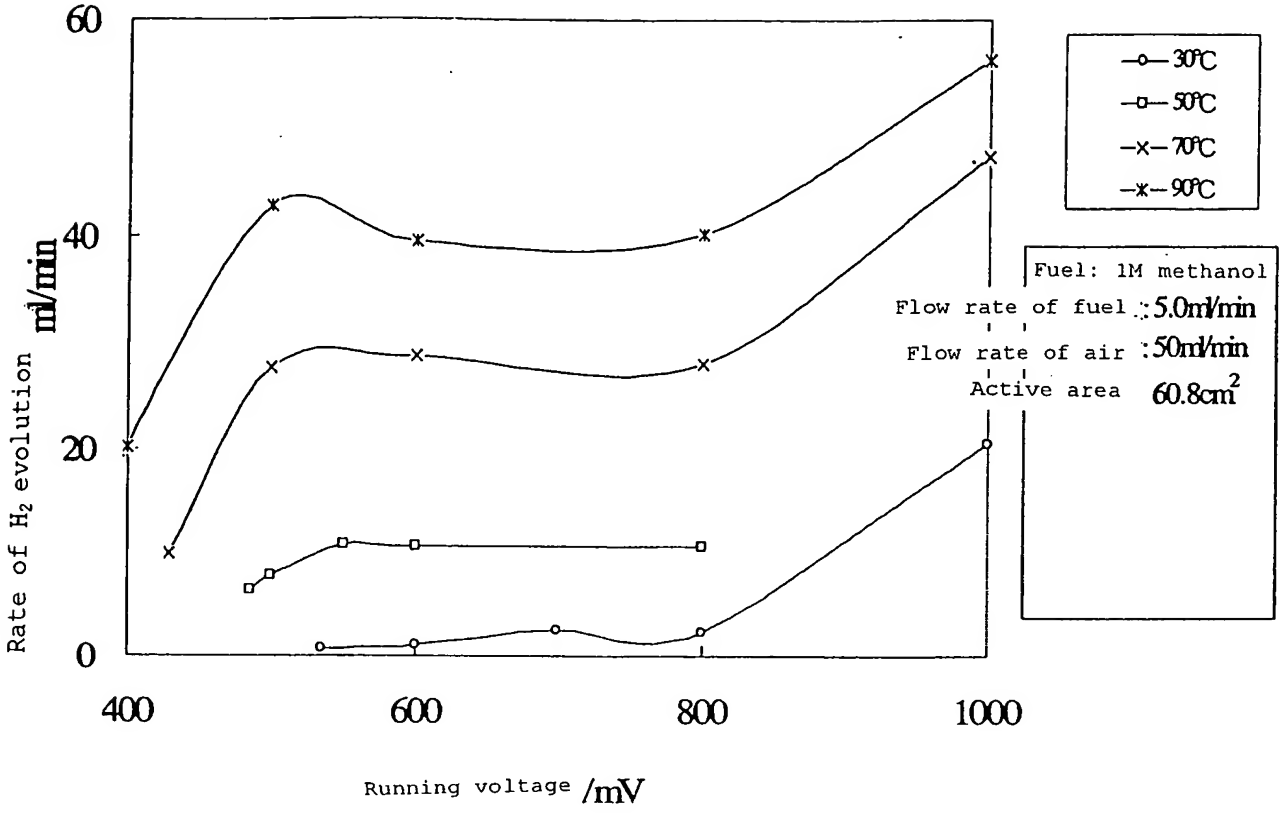

60
40
20
0
Rate of H_2 evolution ml/min
400
600
800
1000
Running voltage /mV
30℃
50℃
70℃
90℃
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of air : 50ml/min
Active area 60.8cm^2

FIG. 21

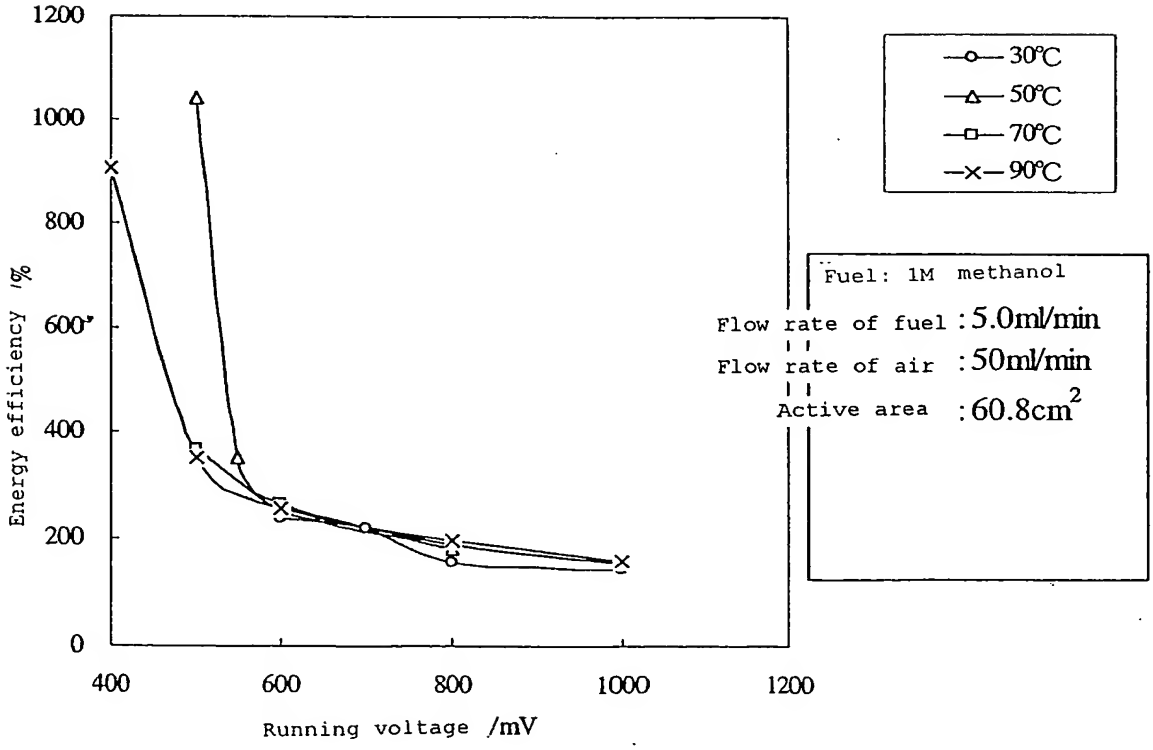

1200
1000
800
600
400
200
0
Energy efficiency /%
400
600
800
1000
1200
Running voltage /mV
30℃
50℃
70℃
90℃
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of air : 50ml/min
Active area : 60.8cm^2

FIG. 22

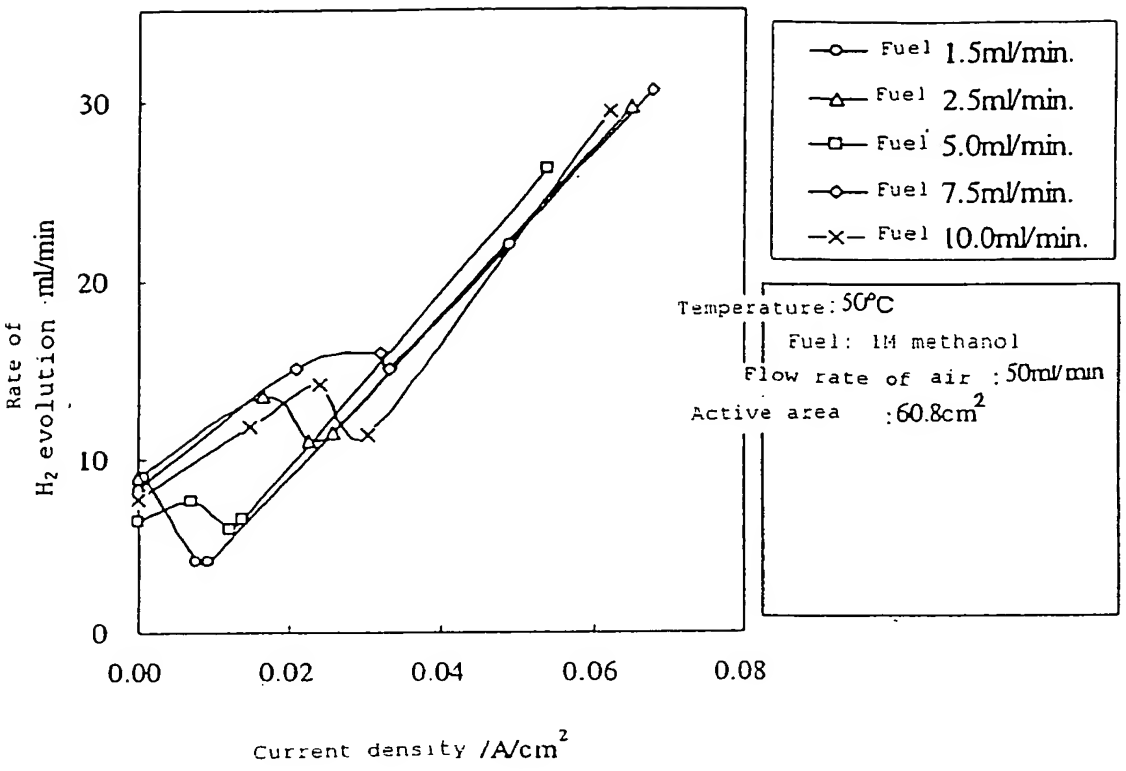

Fuel 1.5ml/min.
Fuel 2.5ml/min.
Fuel 5.0ml/min.
Fuel 7.5ml/min.
Fuel 10.0ml/min.
Temperature: 50°C
Fuel: 1M methanol
Flow rate of air : 50ml/min
Active area : 60.8cm²
Rate of H₂ evolution ml/min
0
10
20
30
0.00
0.02
0.04
0.06
0.08
Current density /A/cm²

FIG. 23

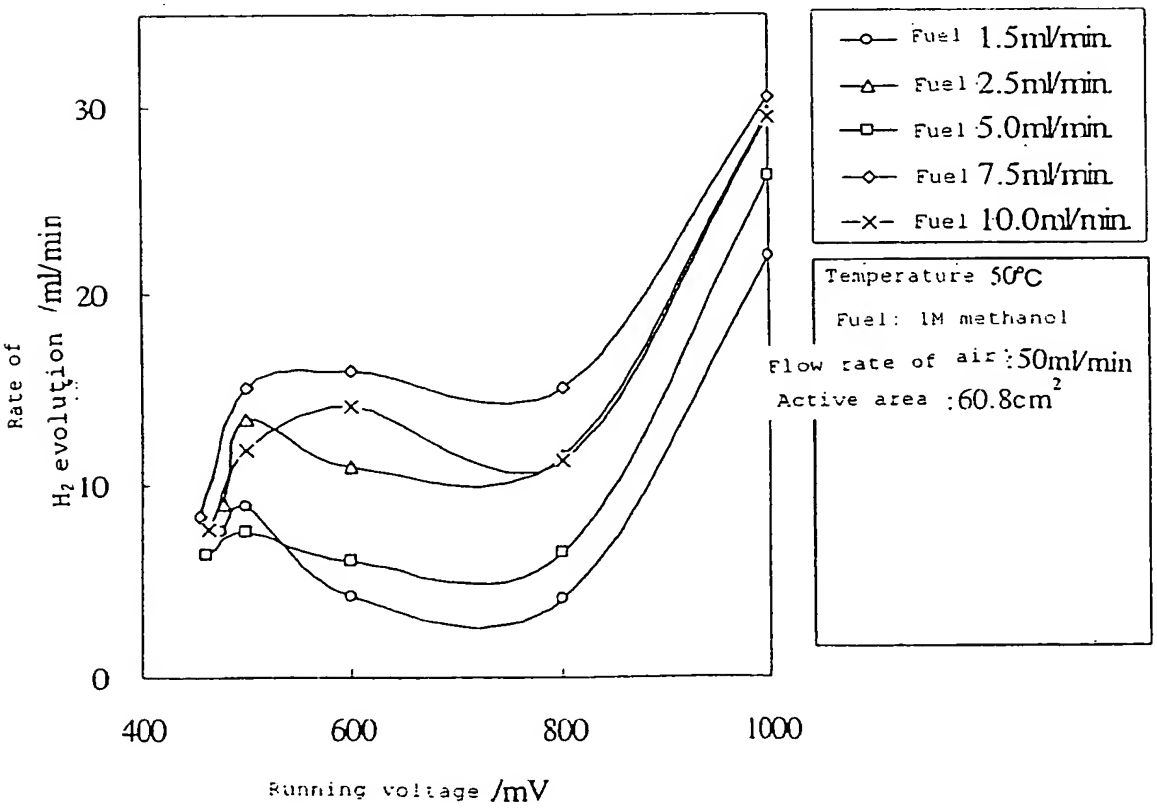

Fuel 1.5ml/min.
Fuel 2.5ml/min.
Fuel 5.0ml/min.
Fuel 7.5ml/min.
Fuel 10.0ml/min.
Temperature 50°C
Fuel: 1M methanol
Flow rate of air : 50ml/min
Active area : 60.8cm²
Rate of H₂ evolution /ml/min
0
10
20
30
400
600
800
1000
Running voltage /mV

FIG. 24

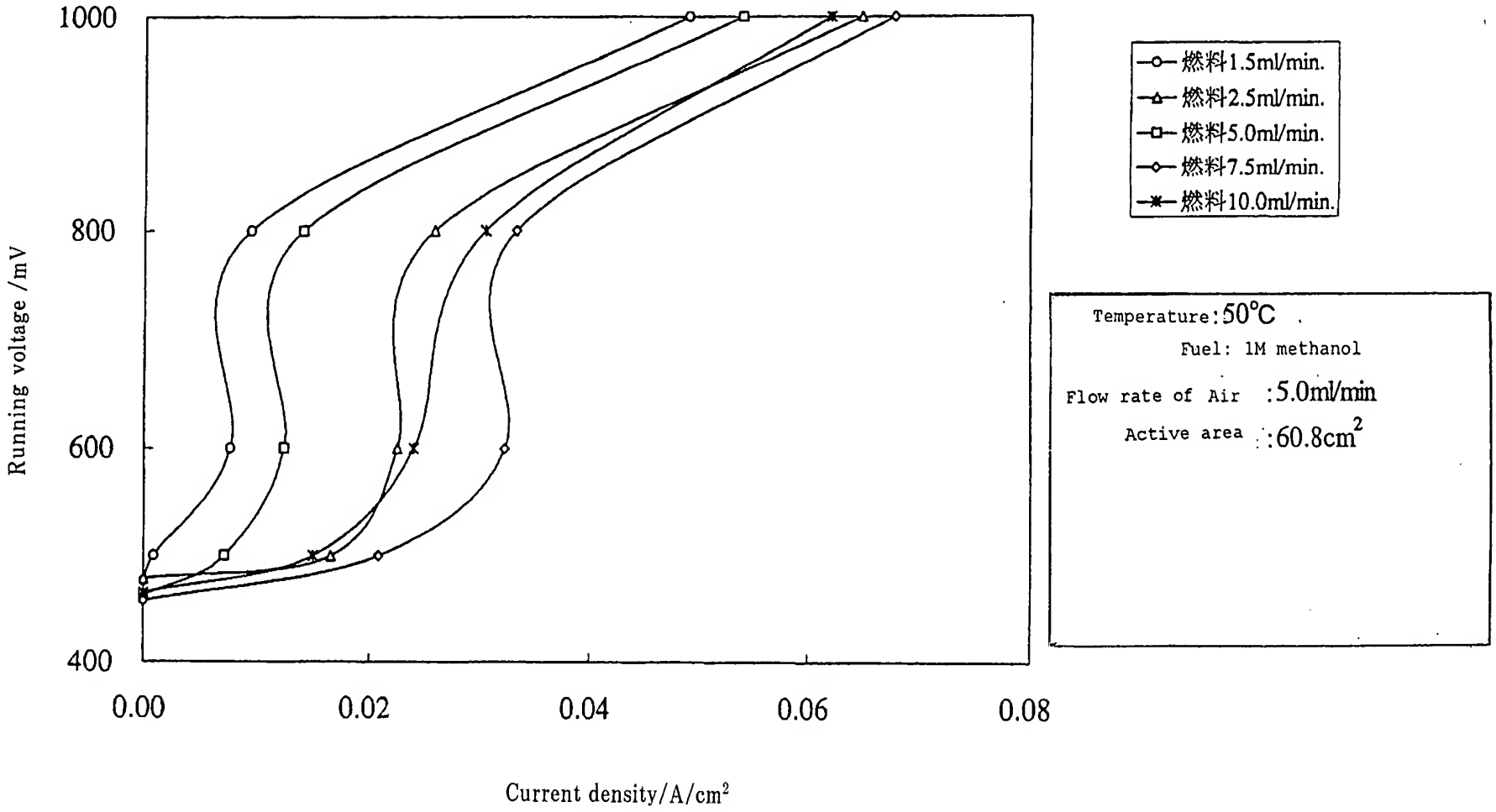

1000
800
600
400
Running voltage /mV
0.00
0.02
0.04
0.06
0.08
Current density/A/cm²
燃料1.5ml/min.
燃料2.5ml/min.
燃料5.0ml/min.
燃料7.5ml/min.
燃料10.0ml/min.
Temperature:50°C
Fuel: 1M methanol
Flow rate of Air :5.0ml/min
Active area :60.8cm²

FIG. 25

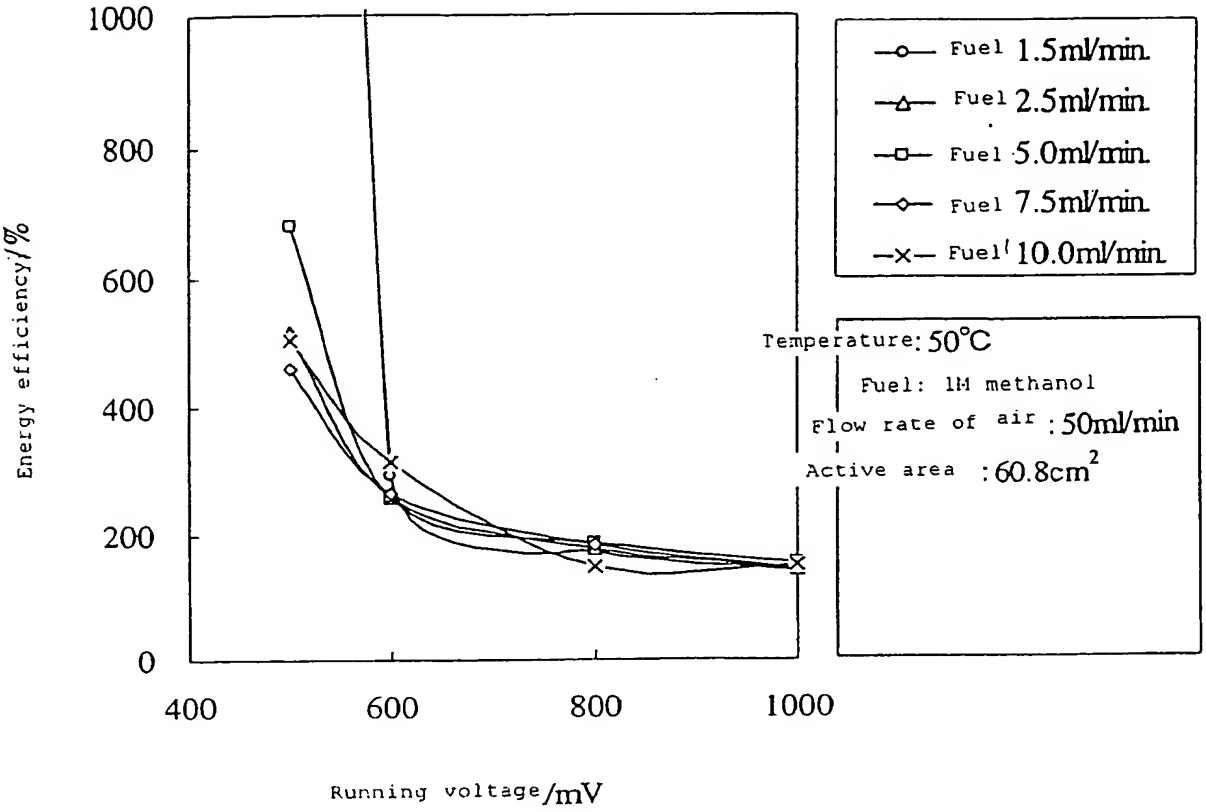

1000
800
600
400
200
0
400
600
800
1000
Energy efficiency/%
Running voltage/mV
Fuel 1.5ml/min.
Fuel 2.5ml/min.
Fuel 5.0ml/min.
Fuel 7.5ml/min.
Fuel 10.0ml/min.
Temperature: 50°C
Fuel: 1M methanol
Flow rate of air : 50ml/min
Active area : 60.8cm²

FIG. 26

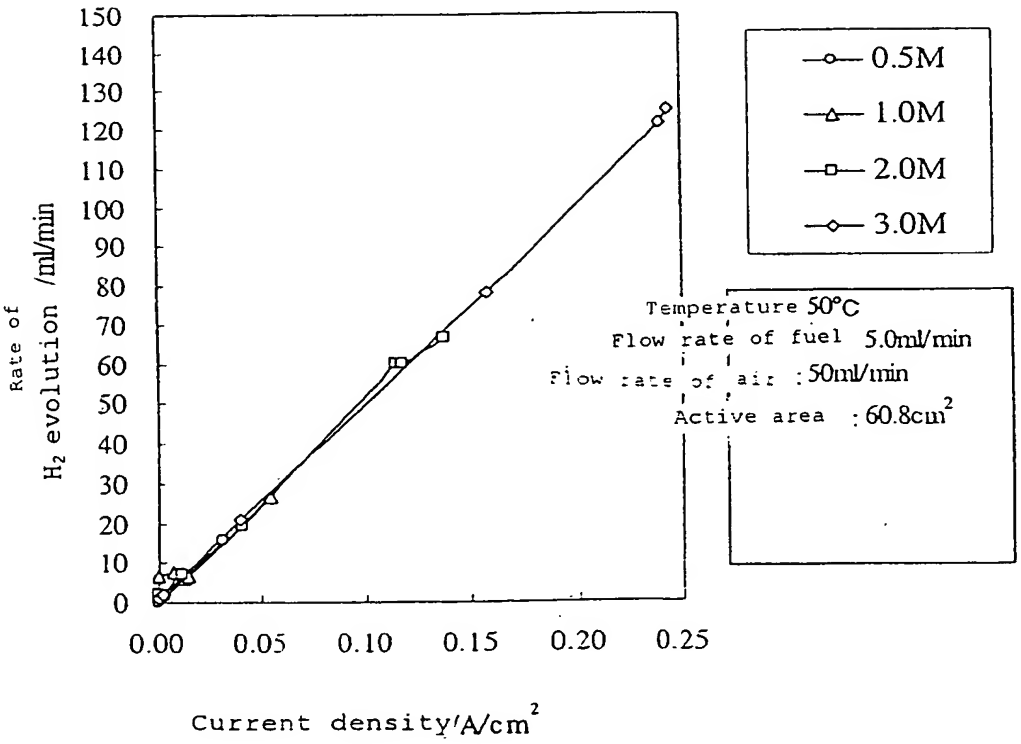

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.00
0.05
0.10
0.15
0.20
0.25
Rate of H₂ evolution /ml/min
Current density/A/cm²
0.5M
1.0M
2.0M
3.0M
Temperature 50°C
Flow rate of fuel 5.0ml/min
Flow rate of air : 50ml/min
Active area : 60.8cm²

FIG. 27

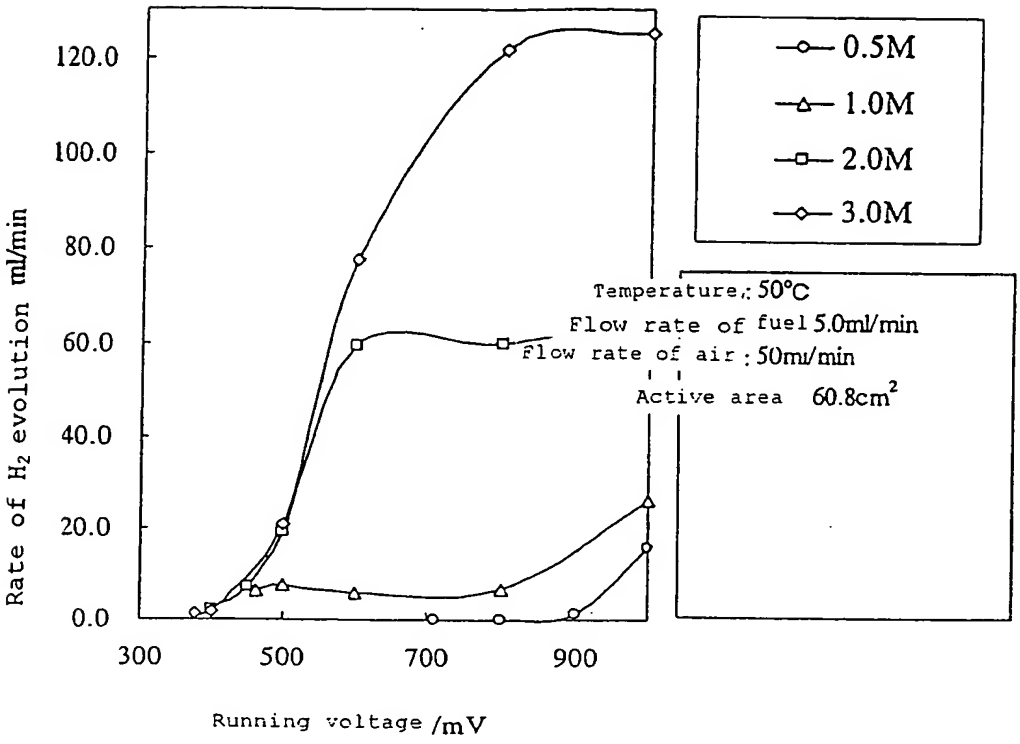

120.0
100.0
80.0
60.0
40.0
20.0
0.0
300
500
700
900
Rate of H_2 evolution ml/min
Running voltage /mV
0.5M
1.0M
2.0M
3.0M
Temperature : 50°C
Flow rate of fuel 5.0ml/min
Flow rate of air : 50ml/min
Active area 60.8cm^2

FIG. 29

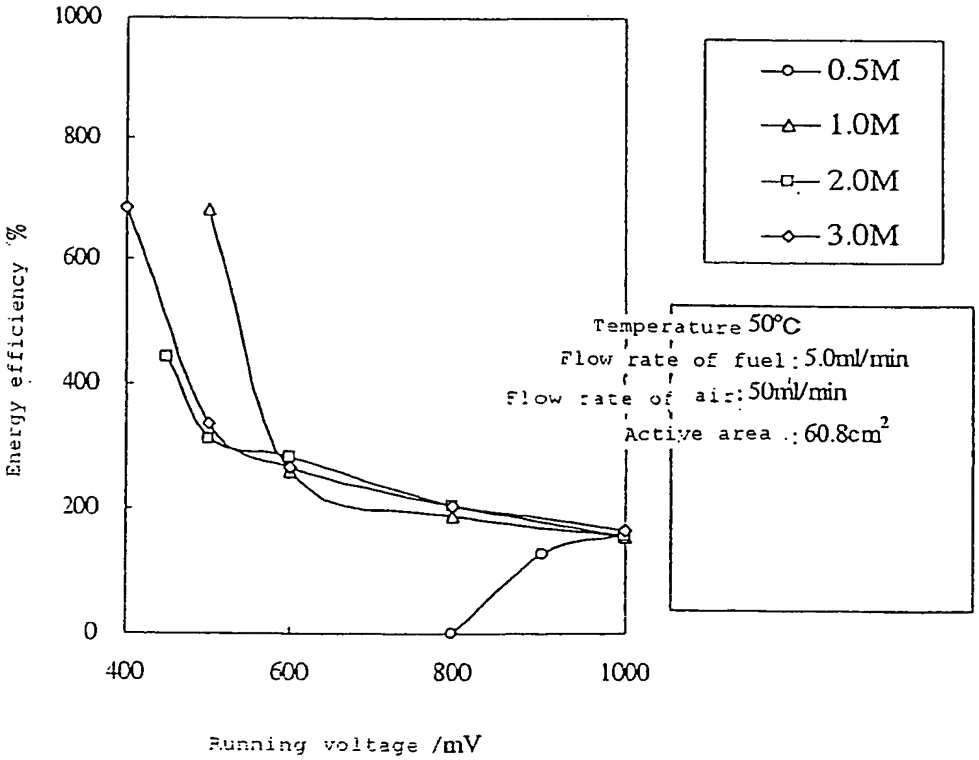

1000
800
600
400
200
0
400
600
800
1000
Energy efficiency %
Running voltage /mV
0.5M
1.0M
2.0M
3.0M
Temperature 50°C
Flow rate of fuel : 5.0ml/min
Flow rate of air : 50ml/min
Active area : 60.8cm^2

FIG. 28

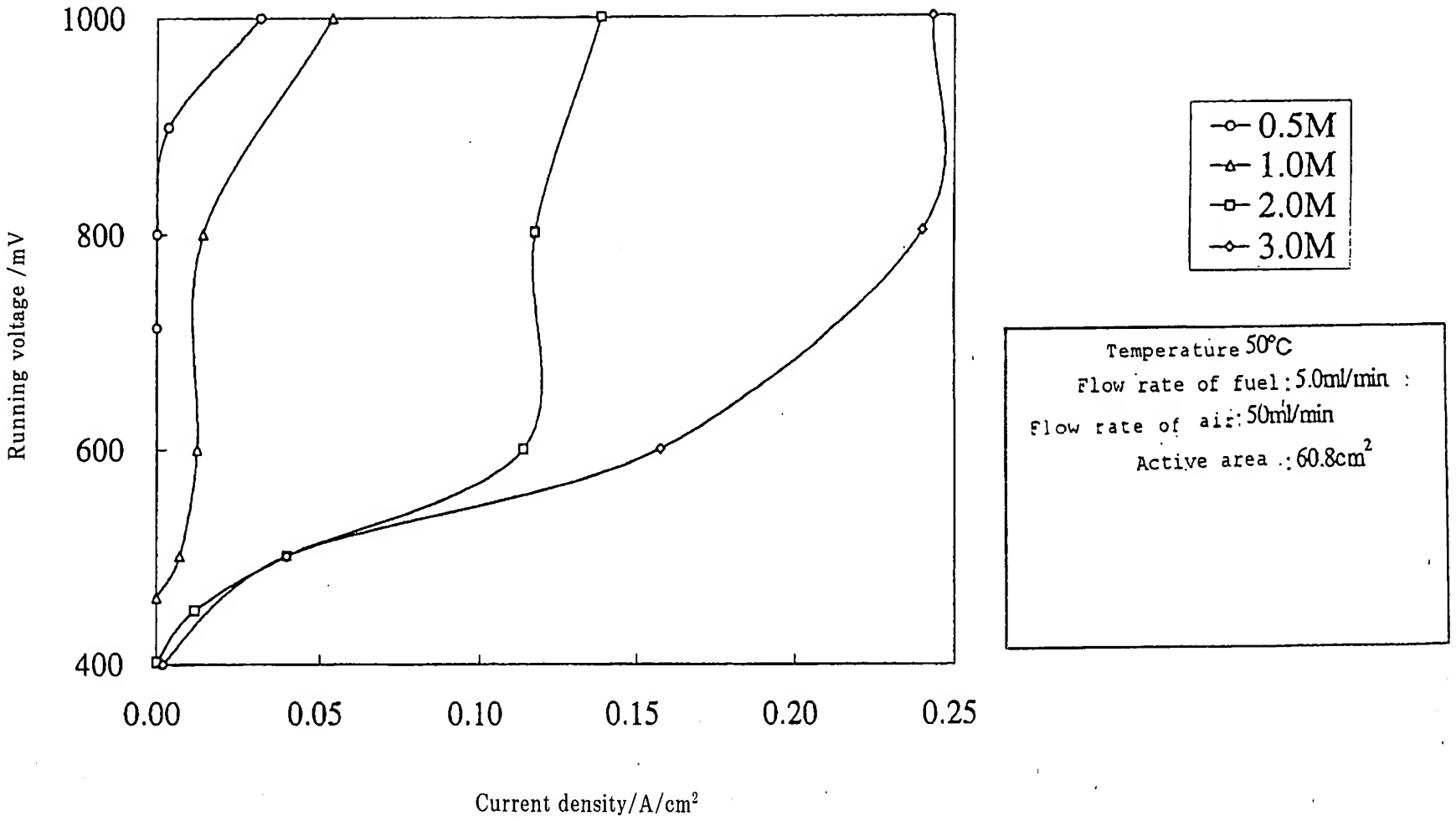

1000
800
600
400
Running voltage /mV
0.00
0.05
0.10
0.15
0.20
0.25
Current density/A/cm²
0.5M
1.0M
2.0M
3.0M
Temperature 50°C
Flow rate of fuel: 5.0ml/min
Flow rate of air: 50ml/min
Active area : 60.8cm²

FIG. 30

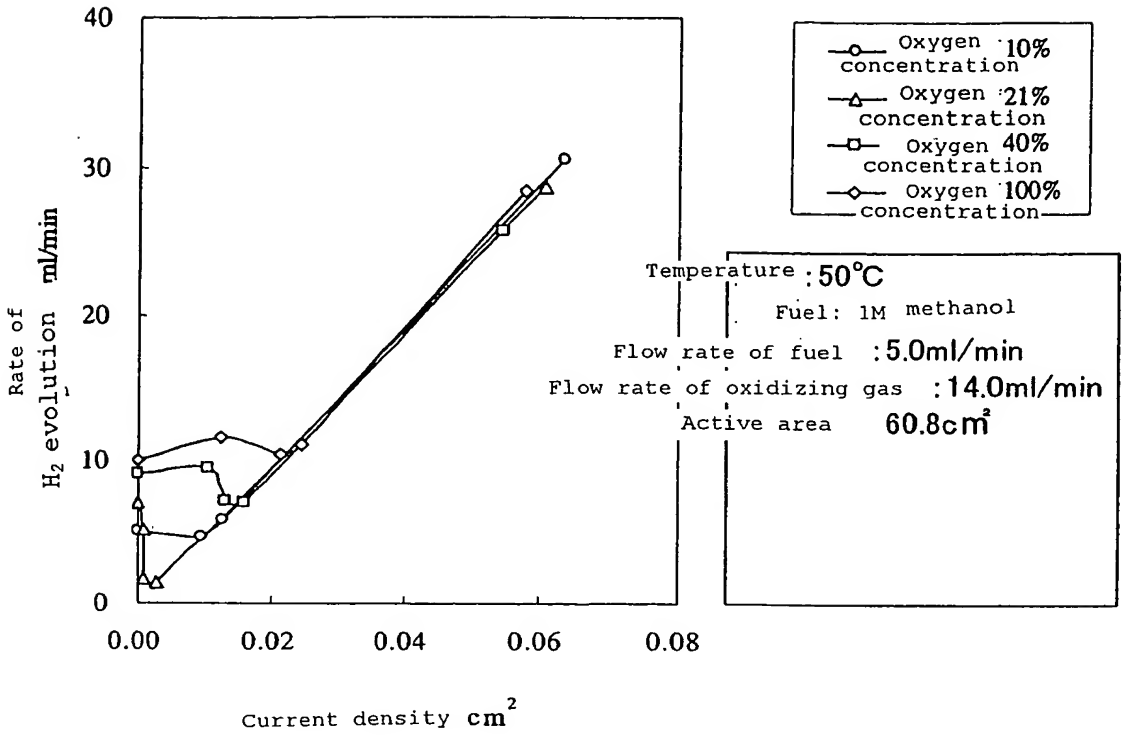

Oxygen concentration 10%
Oxygen concentration 21%
Oxygen concentration 40%
Oxygen concentration 100%
Temperature : 50°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of oxidizing gas : 14.0ml/min
Active area 60.8cm²
Rate of H2 evolution ml/min
Current density cm²
0
10
20
30
40
0.00
0.02
0.04
0.06
0.08

FIG. 31

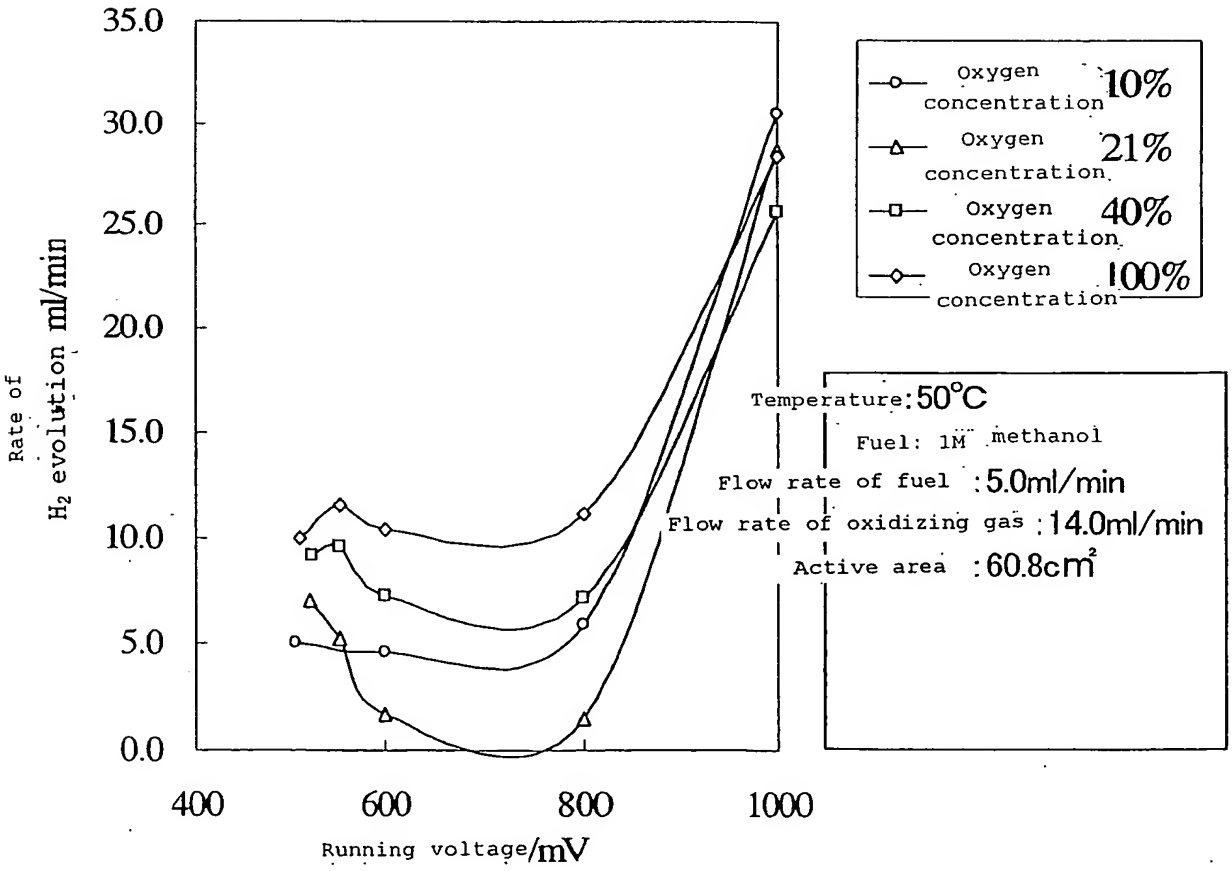

Oxygen concentration 10%
Oxygen concentration 21%
Oxygen concentration 40%
Oxygen concentration 100%
Temperature: 50°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of oxidizing gas : 14.0ml/min
Active area : 60.8cm²
Rate of H2 evolution ml/min
Running voltage/mV
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
400
600
800
1000

FIG. 32

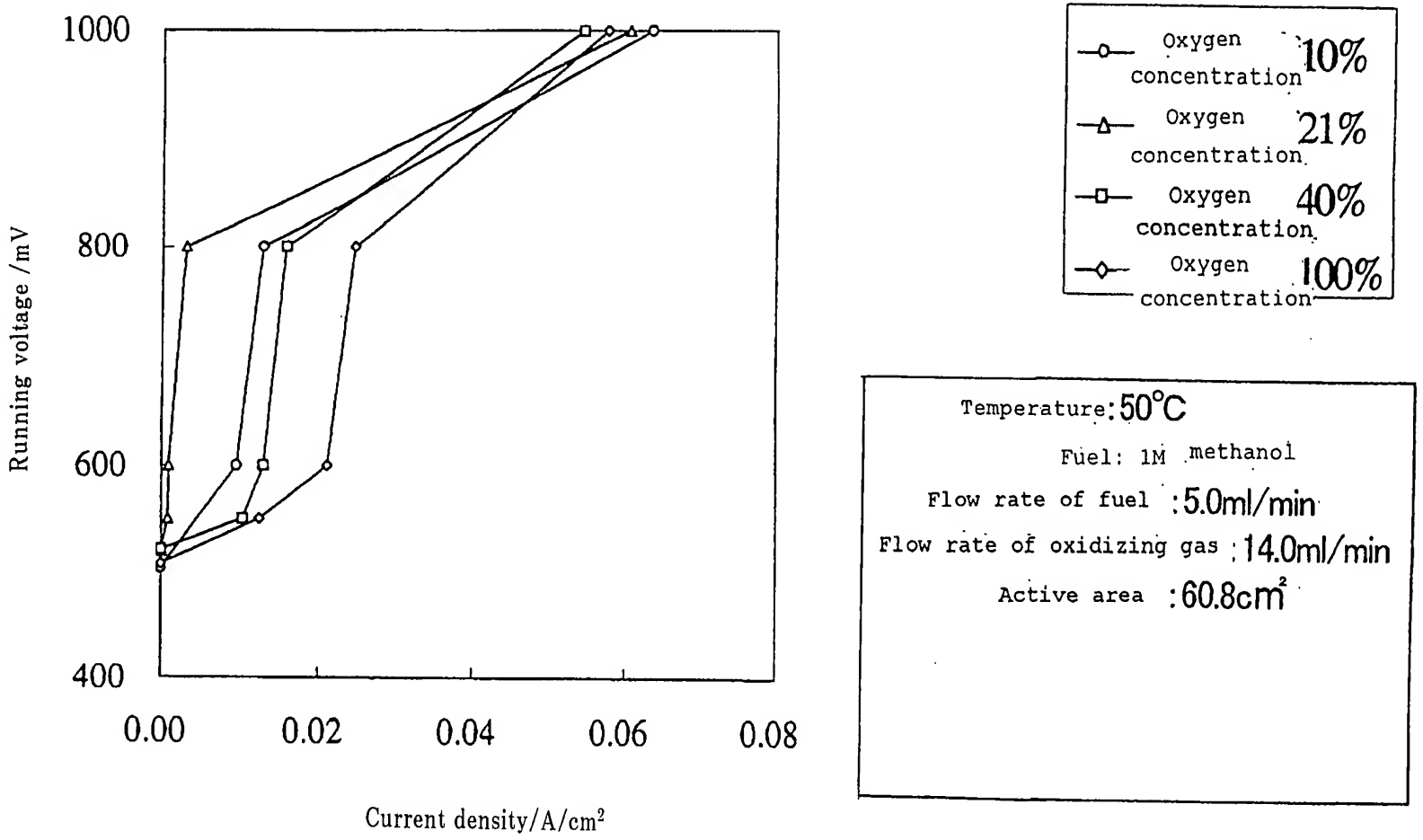

1000
800
600
400
0.00
0.02
0.04
0.06
0.08
Running voltage /mV
Current density/A/cm²
Oxygen concentration 10%
Oxygen concentration 21%
Oxygen concentration 40%
Oxygen concentration 100%
Temperature: 50°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of oxidizing gas : 14.0ml/min
Active area : 60.8cm²

FIG. 33

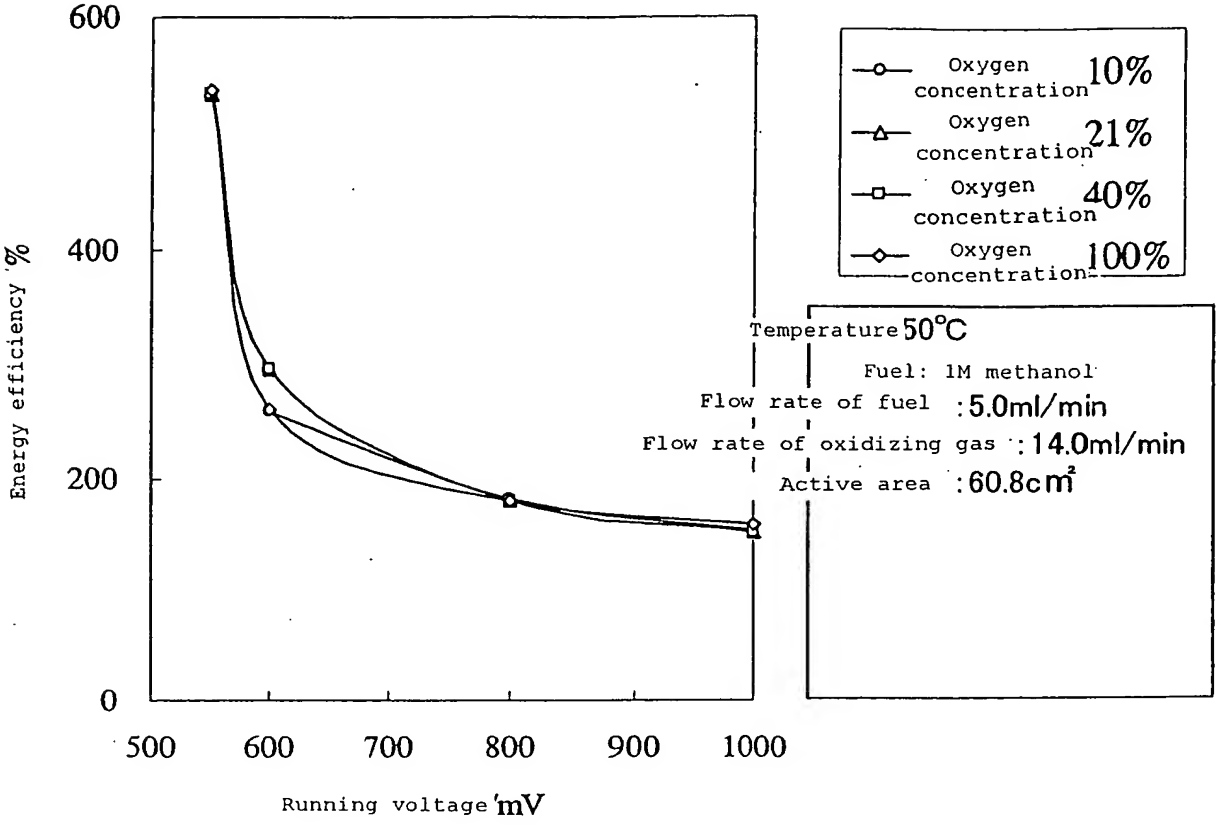

600
400
200
0
Energy efficiency %
500
600
700
800
900
1000
Running voltage mV
Oxygen concentration 10%
Oxygen concentration 21%
Oxygen concentration 40%
Oxygen concentration 100%
Temperature 50°C
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Flow rate of oxidizing gas : 14.0ml/min
Active area : 60.8cm²

FIG. 34

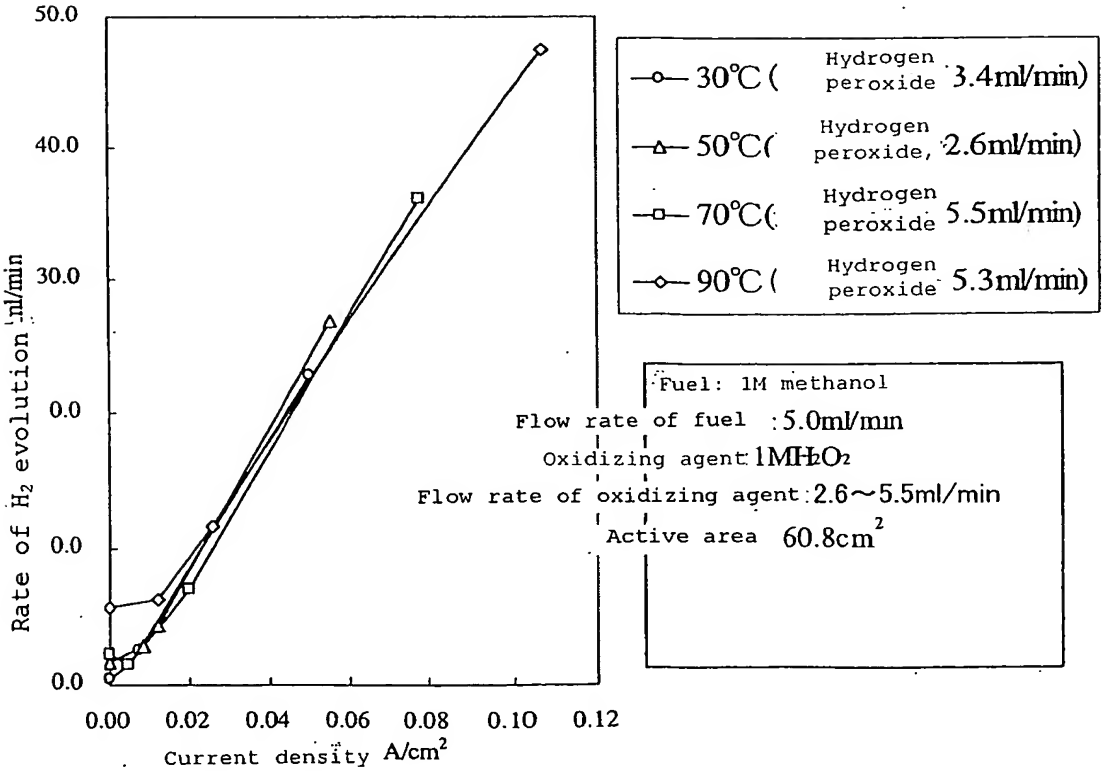

50.0
40.0
30.0
0.0
0.0
0.0
Rate of H2 evolution ml/min
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Current density A/cm²
30°C (Hydrogen peroxide 3.4ml/min)
50°C (Hydrogen peroxide, 2.6ml/min)
70°C (Hydrogen peroxide 5.5ml/min)
90°C (Hydrogen peroxide 5.3ml/min)
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Oxidizing agent: 1MH2O2
Flow rate of oxidizing agent: 2.6~5.5ml/min
Active area 60.8cm²

FIG. 35

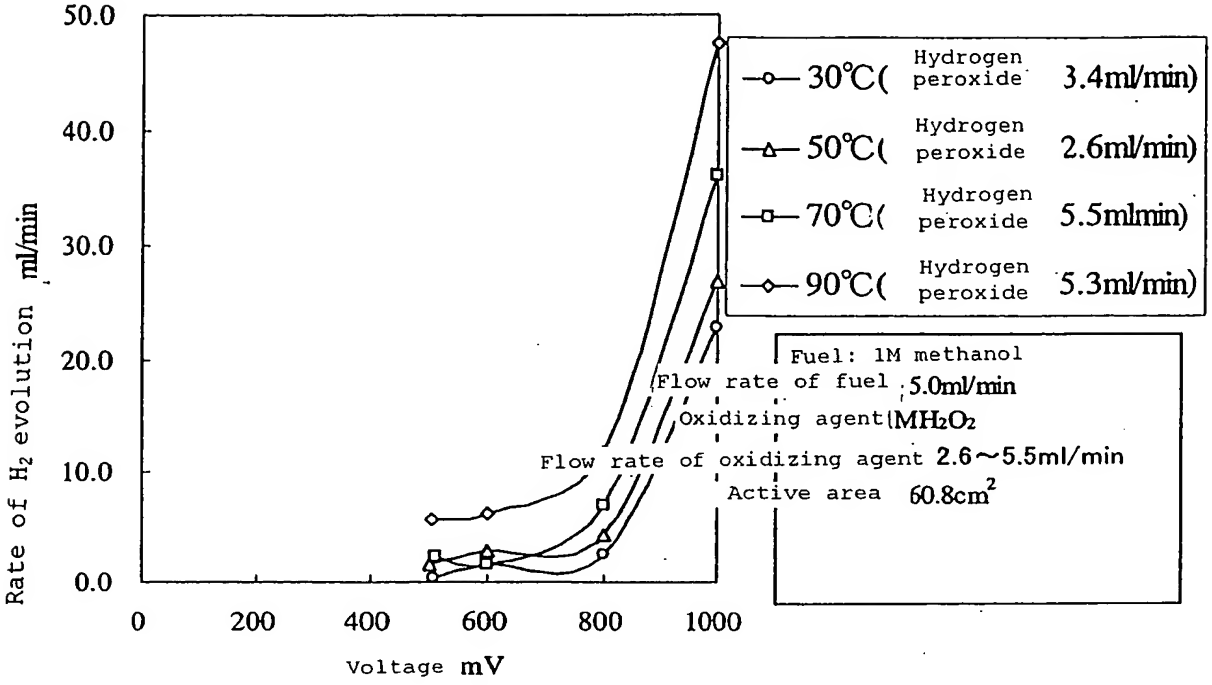

50.0
40.0
30.0
20.0
10.0
0.0
Rate of H_2 evolution ml/min
0
200
400
600
800
1000
Voltage mV
30℃(Hydrogen peroxide 3.4ml/min)
50℃(Hydrogen peroxide 2.6ml/min)
70℃(Hydrogen peroxide 5.5mlmin)
90℃(Hydrogen peroxide 5.3ml/min)
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Oxidizing agent $1MH_2O_2$
Flow rate of oxidizing agent 2.6~5.5ml/min
Active area $60.8cm^2$

FIG. 37

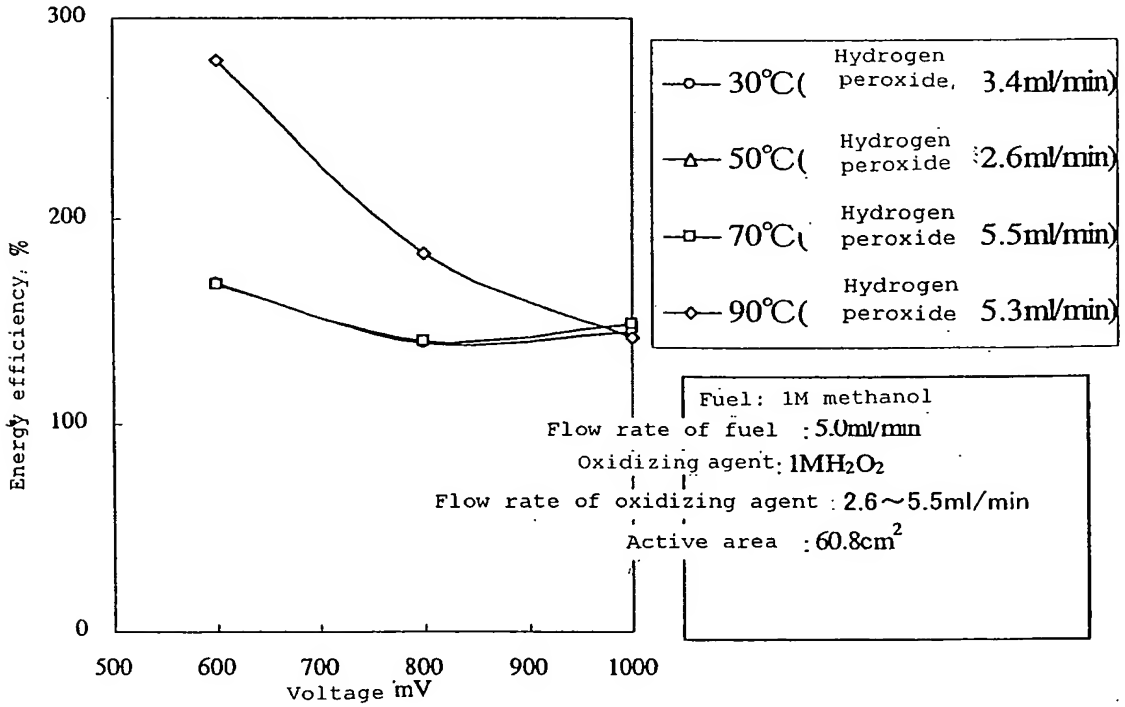
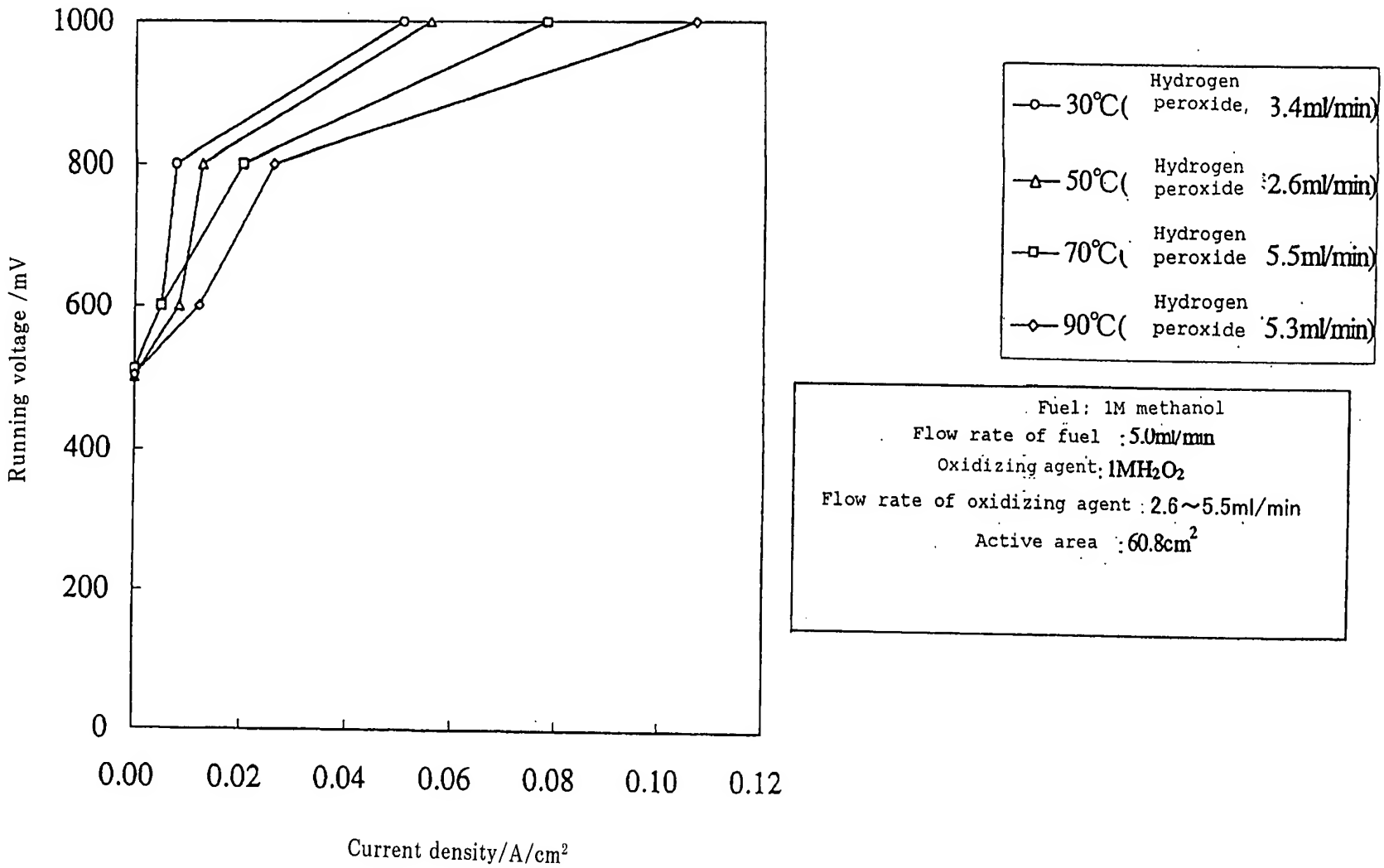

300
200
100
0
Energy efficiency, %
500
600
700
800
900
1000
Voltage mV
30℃(Hydrogen peroxide, 3.4ml/min)
50℃(Hydrogen peroxide 2.6ml/min)
70℃(Hydrogen peroxide 5.5ml/min)
90℃(Hydrogen peroxide 5.3ml/min)
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/min
Oxidizing agent: $1MH_2O_2$
Flow rate of oxidizing agent : 2.6~5.5ml/min
Active area : $60.8cm^2$

FIG. 36


1000
800
600
400
200
0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Running voltage /mV
Current density/A/cm²
30℃(Hydrogen peroxide, 3.4ml/min)
50℃(Hydrogen peroxide 2.6ml/min)
70℃(Hydrogen peroxide 5.5ml/min)
90℃(Hydrogen peroxide 5.3ml/min)
Fuel: 1M methanol
Flow rate of fuel : 5.0ml/mn
Oxidizing agent: 1MH2O2
Flow rate of oxidizing agent : 2.6~5.5ml/min
Active area : 60.8cm2